



Faculty of Sciences

Department of Chemistry and Forensic Sciences

**THE EFFECT OF SUBSTITUENTS ON THE
STABILITY AND FRAGMENTATION OF PARA-
BENZOQUINONE MOLECULAR ANION**

by

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Faculty of Science, BIUST
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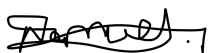
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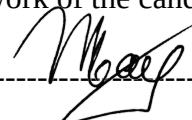
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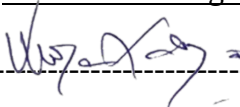
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ABSTRACT

Quinones form a large group of organic compounds with various applications in industry, biological systems, and pharmacology. They can capture an electron with kinetic energy exceeding zero and keep it for a longer time. The principal structure responsible for electron capturing in quinones is the para-benzoquinone, PBQ. Several studies have been carried out on PBQ and its molecular anion, but less attention has been paid to its derivatives upon capturing an electron. As such, the focus of this study is to investigate the effects of substituents on the molecular anion properties of PBQ. These results will fill a void in available data and help in selecting new compounds as possible candidates for the synthesis of new electron acceptors. Both theoretical and experimental work were conducted to obtain the results. Electron donating substituents were found to decrease the stability of the molecular anion and led to the formation of more anion fragments under electron capture negative chemical ionisation mass spectrometry (ECNI-MS) conditions while electron withdrawing substituents showed the opposite effect. The theoretical fragmentation schemes constructed for all dissociation channels in all molecules speculate that most of the fragment anions were formed due to loss of CO and/or C₂H₄ from the molecular anions, sometimes accompanied by migration of H-atom to a nearby or distant C-atom or elimination of H-atom/s. Electron donating derivatives retained several features of the spectra of PBQ itself. In addition to the pronounced molecular anion peaks and [M-CO]⁻, there were other significant peaks at *m/z* 41, 53, 54, 55, 80 and 81 corresponding to the formation of [C₂HO]⁻, [C₃HO]⁻, [C₃H₂O]⁻, [C₃H₃O]⁻, [C₅H₄O/ C₄O₂]⁻ and [C₄HO₂]⁻ respectively with electron donating derivatives. Unlike electron donating derivatives, electron withdrawing derivative's base peaks were due to the formation of Cl⁻ or F⁻. The most common fragment anions apart from Cl⁻ in chlorinated PBQs at *m/z* 41, 53 and 80 corresponds to [C₂HO]⁻, [C₃HO]⁻, and [C₄O₂]⁻, respectively. Density Functional Theory calculations on the electron affinities, reduction potentials and C=O vibrational frequencies, strongly supported the observations noticed in ECNI-MS. The destabilizing effect of electron donating groups decreased the electron affinity, reduction potential and C=O vibrational frequency of PBQ molecular anion while the stabilizing effect of electron withdrawing groups increased them. There was a linear correlation between the response of M⁻ in ECNICI, electron affinities and reduction potentials.

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1 INTRODUCTION

1.1 Background Information On Quinones

Quinones are a broad group of organic compounds derived from aromatic compounds by conversion of an even number of $-\text{CH}=\text{}$ groups into $-\text{C}(=\text{O})-$ groups. The conversion of aromatic compounds involves rearrangement of the double bonds resulting in a fully conjugated cyclic dione structure [1]. Quinone molecules contain two carbonyl groups, $\text{C}=\text{O}$, either on para, meta or ortho positions of the molecule. The para-benzoquinone, **Figure 1.1(a)** and ortho-benzoquinone, **Figure 1.1(b)** are usually the most common quinones available whereas the meta-benzoquinone, **Figure 1.1(c)** is unstable due to its non-planar and highly strained structure [2].

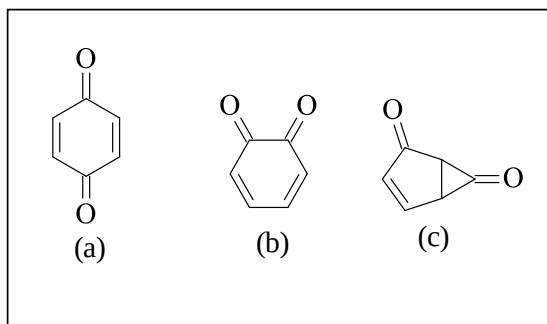


Figure 1.1: Structures of benzoquinone molecules (a) para-benzoquinone, (b) ortho-benzoquinone and (c) meta-benzoquinone.

Besides animals, bacteria, fungi and arthropods, quinones also occur naturally in plants such as *Ranunculaceae*, *Aphodelaceae*, *Fabaceae*, *Ebenaceae* and *Rhamnaceae* [3], [4]. Examples of quinones includes benzoquinones (PBQ), naphthoquinones, anthraquinones, plastoquinones (PQ), ubiquinones (UQ), thymoquinones, embelin, etc.

A wide range of analytical methods has been reported for the determination of quinones in plants, pharmaceutical preparations, as well as in biological samples. Fourier-transform infrared spectroscopy (FTIR) has been used to determine their functional groups [5], mass spectrometry in negative or positive ionisation mode coupled to gas chromatography (GC) or high performance liquid chromatography (HPLC) was used to determine quinones [6] electrochemical experiments to

calculated their reduction potentials [7], [8], [9] and their crystal structures using x-ray diffraction (XRD) [10]. in addition, computational characterization of quinones has also been employed where their structural properties as well as some reactivity and energy properties were determined using Density Functional Theory (DFT) model [11].

Quinones are good electron scavengers, therefore they can capture an additional electron and transfer it to electron seeking species during chemical and biological processes. The basic structure of quinones responsible for accepting electrons is the benzoquinone, more specifically, the para-benzoquinone due to its stability [12].

1.2 Properties of Para-Benzoquinones

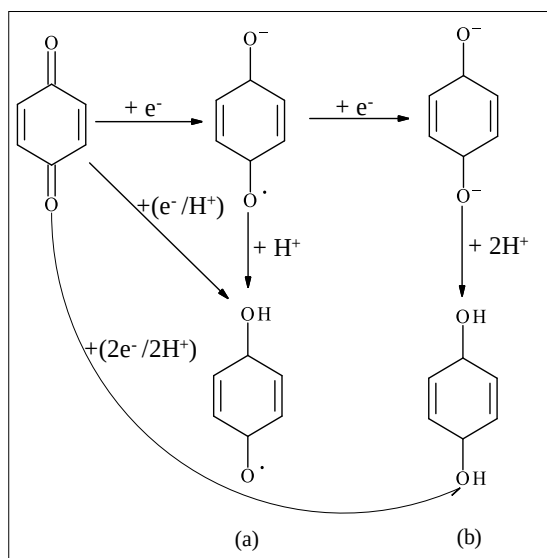
Para-benzoquinone (PBQ), also known as 1,4-benzoquinone, 2,5-cyclohexadiene-1,4-dione or 1,4-cyclohexadienedione is a chemical compound with the formula $C_6H_4O_2$. PBQ is a planar molecule in both neutral and anionic radical form belonging to the D_{2h} point group. The electronic ground states of its anion and neutral species have B_{2g} and ^1A_g symmetries respectively[12][13]. It is a green-yellowish needle-like crystal with a pungent odour resembling that of a chlorine gas. It is very soluble in organic solvents; ethers, alcohols, dichloromethane, acetonitrile, acetone, etc., slightly soluble in petroleum ether and insoluble in water [14]. **Table 1.1** summarises the physical properties of PBQ.

Table 1.1: Properties of para-benzoquinone.

Molecular mass	108.09 g/mol [14]
Melting point	113 °C [14], 116 °C [15]
Boiling point	180 °C [15]
Density	1.318 g/cm ³ [14]
Ionization energy	9.99 eV [16]
Electron affinity	1.89 eV [17]
Dipole moment	0.67 D [18]

1.3 Reactions of Para-Benzoquinone

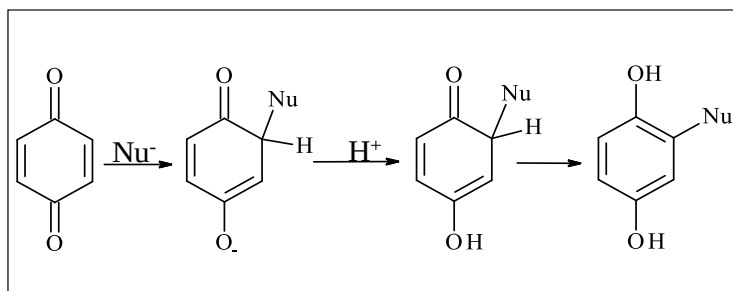
Due to its α,β -unsaturated carbonyl groups, the compound plays a vital role in different reactions such as reversible redox reactions, addition reactions and substitution reactions. As electron capturers, PBQs are excellent electron carriers during redox reactions [19]. As stated, [3], PBQ can undergo electron, proton and/or proton-coupled electron reduction which results in the formation of (a) semi-quinone (SQ) and (b) hydro-quinone (HQ) as illustrated in **Scheme 1.1**.



Scheme 1.1: Illustration of one or two electron reduction yielding (a) semi-quinone (SQ) and (b) hydro-quinone (HQ). Adapted from [3].

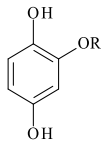
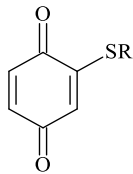
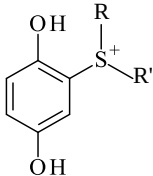
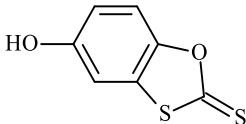
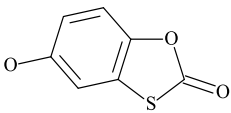
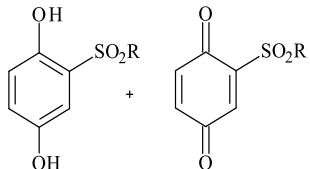
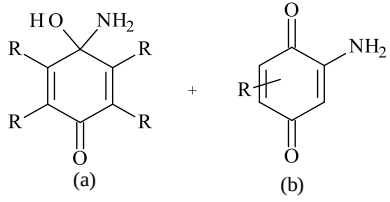
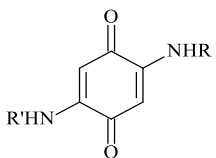
Another chemical reaction of PBQ is observed during nucleophilic addition reaction,

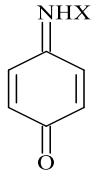
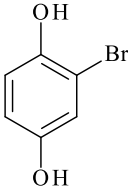
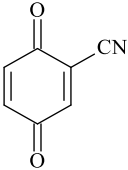
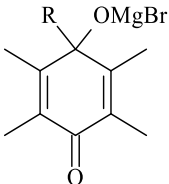
Scheme 1.2, illustrates. PBQ easily reacts with primary and secondary aliphatic or aromatic amines to form disubstituted compounds via a nucleophilic addition reactions [3][20][21]. Several nucleophilic addition reactions of PBQ have been studied [21], and these reactions are summarised in **Table 1.2**.



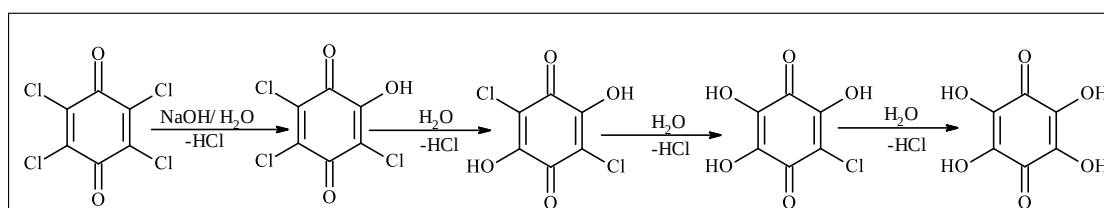
Scheme 1.2: The general nucleophilic addition reaction of PBQ. *Adapted from* [21]

Table 1.2: Nucleophilic addition reactions of para-benzoquinone.

Nucleophile added to PBQ	Product (s) formed
Alcohols (ROH)	
Thiols (RSH)	
Thio ethers (R-S-R')	
Thiolic acids	
Thiocynic acids	
Sulphinic acids & sulphurous salts	
(a) Gaseous NH ₃ (with substituted PBQs) (b) hydrazoic acid (NH ₃)	
Amines (NHR)	

Hydroxylamine/cynamide/ hydrazide ((H ₂ NX) (X= OH, CN, NRR', NHC(O)R	
Halogens (F, Cl, Br, I)	
Hydrogen cyanide (HCN)	
Organometallic compounds (RMgBr)	

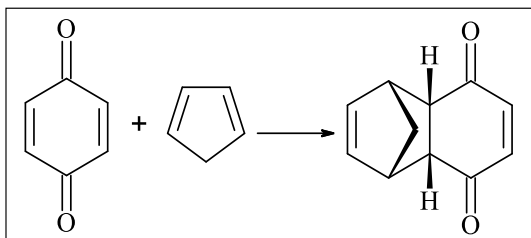
With electron withdrawing groups (EWG) such as halogen, cyanide, and nitrate substituents attached to PBQ, addition reactions may not occur as expected but instead a nucleophilic substitution reaction will take place. EWG increases the electron affinity of PBQ activating the ring towards nucleophilic substitution. An example of a nucleophilic substitution of a quinone is the hydrolysis of halogenated quinones to hydroxyquinone as illustrated in **Scheme 1.3** [22], [21].



Scheme 1.3: Nucleophilic substitution reaction of PBQ. *Adapted from* [21]

PBQ is also an excellent dienophile, which can react with cycloalkenes during [4+2] cycloaddition reaction as illustrated in **Scheme 1.4**. An excellent example is the

reaction between PBQ and cyclopentadiene to give cyclopentadiene quinone adduct which is mostly used as a starting material when synthesising natural products [23], [24].



Scheme 1.4: [4+2] cycloaddition reaction of PBQ with cyclopentadiene. *Adapted from* [24]

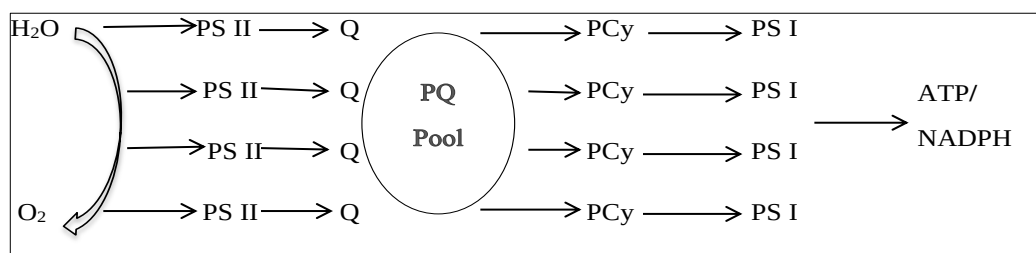
1.4 Applications of PBQ

1.4.1 Biological and pharmaceutical application

PBQ plays a very significant role as antioxidant, anti-biotics, anti-tumor, anti-malarial, anti-neoplastic, anti-coagulant, herbicides, anti-inflammatory, anti-viral activities, fungicides, plant growth regulators etc. [3], [4], [21]. Plants such as black cumin seeds (*Nigella sativa*) have been found to have thymoquinones, which have antitumor activities while embelin, duroquinone and thymoquinone show antioxidant activities, and are good for treating diabetes, oxidative stress, atherogenesis and hyperlipidaemia. They increase the amount of cardiac creatine kinase in the brain, muscles and the heart, and can therefore be used to synthesise drugs that protect against chronic disease [20]. The anti-inflammatory activity of quinones was also found in ubiquinones, thymoquinone, and embelin. These quinones have the potential to increase the amount of collagen while decreasing the level of myeloperoxidase and phospholipase and suppressing the production of nitrogen oxide in human body cells [3], [20], [25]. The anti-bacterial activity of quinones, ignitor activity to pregnancy and anti-inflammatory properties of these compounds have also been reported [25]. Findings shows that embelin has a significant anti-bacterial activity against gram-positive bacteria. Naphthoquinones have also shown to have great potential as anti-fungal agents with high activities [26] while ubiquinones (UQ) have been discovered to have an antioxidant activity. UQ have a neuroprotection effect due to increased levels of antioxidant enzyme,

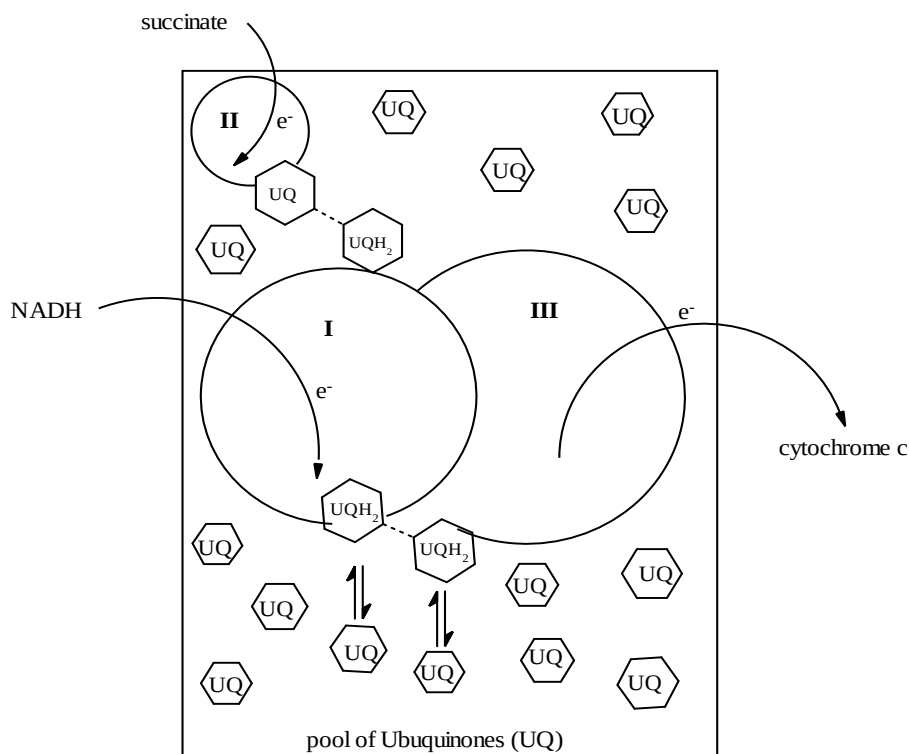
which suppresses the gene associated with human cell signalling, metabolism, and transport. It also safeguard the system from protein degradation, DNA oxidation and lipid peroxidation which can be responsible for the initiation of several diseases (e.g., trauma and stroke) [20].

PBQs have a noticeable application in biological functions such as photosynthesis and respiration. For example, plastoquinones (PQ) are involved in electron transfer (ET) and proton transfer (PT) during photosynthesis in the thylakoids of the chloroplasts or cellular membrane of bacteria, **Scheme 1.5** illustrates. PQ attracts electrons and protons from the stroma. It is then reduced to plastoquinol (PQH₂) which is in turn be oxidised to PQ at the cytochrome b₆F. This process generates energy in the form of nicotinamide adenine dinucleotide phosphate and adenosine triphosphate, NADPH/ATP which is required during carbon fixation and other endothermic reactions [24], [27]–[29].



Scheme 1.5: Electron transfer during photosynthesis by plastoquinone. *Adapted from* [28].

While plastoquinone transfers electrons during photosynthesis, the Coenzyme Q₁₀ also known as Ubiquinone (UQ) is a co-factor in the electron transfer chain during respiration. UQ is a small, lipid-soluble quinone molecule with redox active moiety and a hydrophobic phospholipids bilayer that can diffuse within and across the inner membrane of the mitochondria [30], [31]. As illustrated in **Scheme 1.6**, UQ transfers electrons from complex I (NADH: Ubiquinone oxidoreductase) and complex II (Succinate: Ubiquinone oxidoreductase) to complex III (cytochrome bc₁) during respiration [32], [33].



Scheme 1.6: Electron transfer during respiration by ubiquinones. *Adapted from [32].*

Nevertheless, PBQs can also be toxic in biological systems as they easily bind to thiols, amines, and hydroxyl groups. These nucleophiles are reactive side groups of lysine, serine, and cysteine in biological systems. As a strong electrophile, PBQ attacks the thiol group of glutathione (GSH) and this reaction results in detoxification [3].

1.4.2 Chemical and industrial application

Traditionally, PBQs were well known to be used in the manufacture of dyes because of their bright colours, but nowadays they have a significant use in industry and scientific laboratories. Due to their special characters of undergoing reversible redox reactions and nucleophilic attack, they are now used as analytical reagents, polymer modifiers, photo resistors, catalysts, chemical intermediates, oxidising agents and tanning agents [4], [21]. PBQs have been found to be excellent chelating agents because they easily bind with heavy metals and this increases the solubility, migration, redistribution and accumulation of heavy metals during water treatments [34]. Another application of PBQs in industry reported is Thio-Diels-Alder reactions of thiochalcones with 1,4-quinones which produces a new class of 4H-

thiopyran derivatives [35]. 4H-thiopyran derivatives constitute a structural unit of several natural products [36]. Para-benzoquinones have also been used during organic synthesis as excellent oxidants. An example is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) which has a high redox potential and is usually used to dehydrogenate steroids, alcohols, phenols and ketones [24]. Furthermore, the redox properties of quinones have found remarkable use in industry. They have been used in the determination of pH, design of electrochemical redox switches, light emitting devices, magnetic materials, energy storage devices (such as redox flow batteries), dye-sensitized solar cells, water-splitting devices, luminophores in photography, optical generators (lasers), liquid crystalline and manufacture of dye [20], [37].

1.5 Statement of the Problem

Para-benzoquinone as the simplest, but key structure in quinones poses unusual, unique properties that depend on its ability to capture an extra electron. Due to this unique properties, quinones participate in many important processes, such as electron transfer in biological systems[6], [17], [38]. Even though PBQ has been intensively studied for several years, a detailed investigation of its derivatives has been given less attention. The core problem this study intends to investigate is whether substituents affect the stability of PBQ molecular anion and if there are possibilities of formation of fragmental anions during ionisation while correlating the response of molecular anion to the molecular properties of PBQs.

1.6 Aim and Objectives

1.6.1 General aim

The main purpose of this study was to understand the effects of substituents on the negative ion properties of para-benzoquinone (PBQ).

1.6.2 Specific objectives

To achieve the above-mentioned aim, several specific objectives were addressed, and these are as follows,

1. To understand and quantify the relationship between structures of differently substituted benzoquinone molecules and their ability to form molecular anion.
2. To explore possible fragmentation pathways of PBQs during electron capture negative chemical ionisation.
3. To calculate the molecular properties of PBQ molecules under study, e.g., reduction potentials, electron affinities, geometrical parameters, and vibrational frequencies and then investigate the effect brought by substituents on these molecular properties.
4. To investigate the relationship between electron affinities, reduction potentials and the signal intensity of molecular anions in ECNCI-MS.

1.7 Hypothesis

The interaction between a neutral PBQ molecule and an electron leads to the formation of a molecular anion. Stable molecular anions can be detected under mass spectrometry. Substituents have a major effect on the molecular properties of PBQ and as a result, they affect the stability of the molecular anion. Electron donating substituents are expected to decrease the stability of the molecular anion and lead to the formation of lots of fragment anions under mass spectrometry conditions while electron withdrawing substituents show the opposite effect.

1.8 Significance of the Study

The ability of PBQs to stabilize upon capturing additional electrons correlates well with their role in electron transport mechanisms in biological systems. For this reason, more extensive data obtained in this study will provide more detailed information on the substituent effect relative to electron attachment properties of PBQ derivatives and this will fill a void in available data on quinone compounds. In addition, these findings will also provide basic information on physical laws concerning interactions between electrons and PBQ molecules. This will help in selecting new compounds as possible candidates for the synthesis of new electron acceptors and as a result, opening a much wider door for applications of PBQs in various fields, such as, in drug discovery.

2 LITERATURE REVIEW

This chapter exposes available relevant literature on different techniques, methods and theories that have been used to study and understand the negative ion properties of para-benzoquinone (PBQ). The effect of substituents on the stability of the PBQ molecular anion is also reviewed.

Quinones form a large group of organic compounds and are widely available in nature, mainly in plants, fungi, and bacteria. This class of compounds has various properties and applications which have been widely reviewed [3], [4], [20], [25], [28], [37], [39]. Their importance ranges from biological, medicinal, organic, and industrial application. The fundamental property of quinone chemistry is their ability to undergo reduction easily, hence their property as excellent oxidizing or dehydrogenating agents. They can easily capture an additional electron with kinetic energy exceeding zero and keep it for a longer time. This is the reason they serve as vital links in biological oxidative systems [6], [17]. The central moiety liable for accepting electrons in quinones is the para-benzoquinone.

The negative ion properties of PBQ have been explored with a range of experimental methods. These include electron swarm experiments [38], electron transfer and SF₆ scavenger techniques (collisional ionization techniques) [17] and the use of static magnetic sector mass spectroscopy to study the resonance electron capture by molecules of PBQ [6]. In both experimental studies, a long-lifetime (30 μ s) negative ion of PBQ was observed at 2.1eV. At this relatively high energy the lifetimes of temporary negative ion states are usually in femto-pico seconds range [40]. In addition to the 5 types of fragment anions (m/z 82, 80, 79, 41 and 25) observed in [17], 19 more types of low intensive fragmental anions were revealed when a static magnetic sector mass spectrometer was used. The fragmentations were postulated to be due to either direct bond breakage, opening of the molecular anion ring accompanied by migration of a hydrogen to a neighbouring carbon atom or migration of a hydrogen atom to a distant carbon atom [6]. The existence of a metastable anion of PBQ was also confirmed by electron transmission spectroscopy studying the time resolved electron energy loss from PBQ [40], [41]. The negative ion state of PBQ was also investigated using frequency resolved photoelectron

imaging [42], photoelectron spectroscopy [13], [43] and time resolved photoelectron spectroscopy [12].

The electronic structure of PBQ and its anion has further been assessed through several quantum chemical models. Most of the theoretical studies were performed using semi-empirical methods [44]–[46], even though there are published *ab initio* calculations [47]–[53]. Both methods have revealed that the ground state of the PBQ anion has D_{2h} equilibrium geometry and is formed by electron attachment to the lowest π^* molecular orbital, b_{2g} . Furthermore, the theoretical calculations have revealed that the electron attachment to neutral PBQ is exothermic with electron affinity of 1.86 eV [52], or 1.88 eV [54]. These values are in good agreement with the experimental value of 1.86 eV [13] and 1.89 eV [17]. Regardless of the large positive electron affinity of PBQ, an electron easily attaches to the neutral molecule via excited electronic states of its anion. Excited states are generated when an electron is promoted from a doubly occupied π orbital to π^*_{SOMO} orbital ($^2B_{3u}$ state) or when an electron is promoted from the π^*_{SOMO} orbital to π^* orbital (^2A_u state) forming two long-lived resonance states with adiabatic electron affinities of 2.9 eV and 2.5 eV respectively, [52], as shown in **Figure 2.1**. The lowest excited state (at 2.5 eV) which is about 0.7 eV above the ground state of the anion is expected to be an entry state for electron attachment in redox processes involving quinones [53], [55].

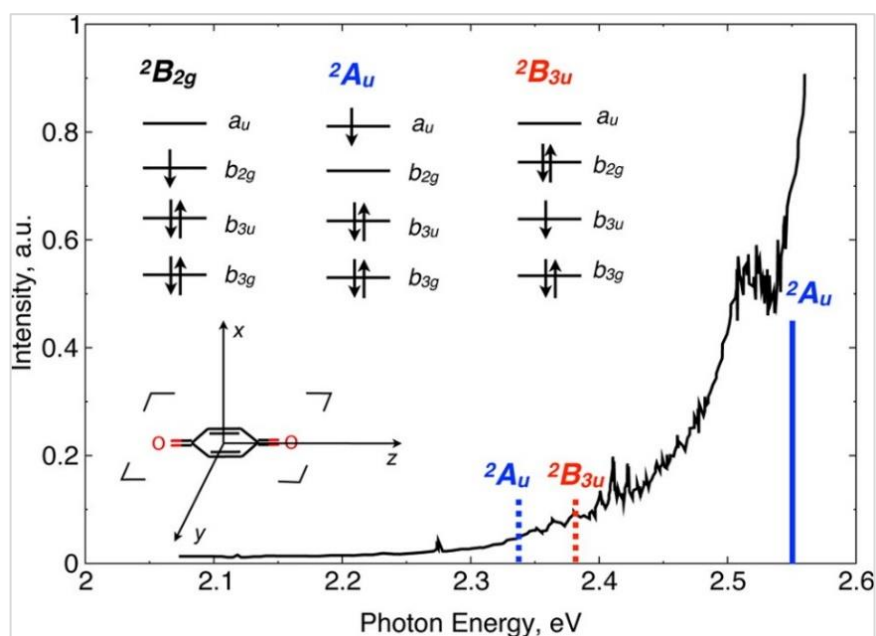


Figure 2.1: Photodetachment spectrum of PBQ anion. Vertical and adiabatic excitation energies to ^2A_u and $^2B_{3u}$ states, are shown as solid and dotted bars, respectively. The vertical excitation energy to the $^2B_{3u}$ state is 2.91eV. Adapted from [52].

Even though PBQ and its anion have been extensively studied, less attention has been given to its derivatives. Even so, stabilization, fragmentation and rearrangement of tetrafluoro PBQ [55] and the formation of negative ions from halogenated PBQs' after interacting with free electrons from 0-10 eV have been conducted [15]. Furthermore, DFT calculations on the electron affinities of quinone derivatives have been published [47], [48], [50], [51]. The results from all the reviews show that halogenated PBQs easily reduce to form very stable molecular anions with high positive electron affinities.

As such, the focus of this study was to investigate and understand the effect of substituents on the negative ion properties of para-benzoquinone (PBQ). To achieve this, both quantum chemistry calculations and experimental studies are used. Experimentally, gas chromatograph coupled to an electron capture negative chemical ionization mass spectrometer (GC-ECNCI-MS) will be used to determine the relationship between the molecular anion of substituted PBQs and their ECNCI-MS response.

3 THEORY, MATERIALS AND METHODS

Here the focus will be on the use of appropriate techniques and methods used to extract data, which when analysed will help to draw interpretations from specific phenomena. It will give a general strategy of how the intended objectives are achieved. In addition to materials, methods and experimental procedures, the chapter will also cover on the theoretical backgrounds of all the experimental and computational techniques involved. A detailed information on the theories, laws and postulates adapted on all the technologies or techniques used in this study will be discussed here. This includes the ionisation techniques used on gas chromatography-mass spectrometry, cyclic voltammetry and quantum chemistry calculations of the electron capture negative chemical ionisation mass spectra, electron affinities, geometrical parameters, and vibrational frequencies.

3.1 Theoretical Backgrounds

3.1.1 Gas chromatography-mass spectrometry (GC-MS)

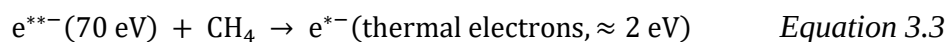
Mass spectrometry as one of the powerful analytical techniques used for both qualitative and quantitative analysis was used for data acquisition. Both electron impact ionisation (EI) and electron capture negative chemical ionisation (ECNCI) were carried out in this study. EI is the most common ionisation technique used in mass spectrometry. This technique involves the collision of energetic electrons (70 eV) produced by a hot filament with the vaporized neutral molecules in the ion source. These electrons can either effect ionisation of an organic molecule via resonance to form a molecular radical cation, $M^{\bullet+}$ or they may cause the molecular ion to break forming an even electron stabilized cation, X^+ and uncharged free radical, $Y^{\bullet}$ as shown in **Equation 3.1** and

Equation

3.2. The uncharged free radical will not show in the mass spectrum since it bears no charge.



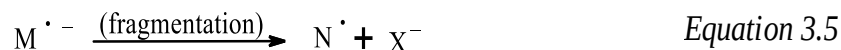
ECNCI is the best technique for studying the electron capture capabilities of organic compounds [56]–[58]. It is very sensitive and selective to electrophilic organic compounds with high electron affinity or electron capture capacity such as benzoquinones hence the main reason for using it in this study [57], [59]. In our study, methane gas (CH₄) was used as a reagent gas to collide with 70 eV electrons from the filament to produce thermal electrons as shown in **Equation 3.3**.



The thermal electrons produced in **Equation 3.3** may attach to the neutral molecule, M, and occupy the lowest unoccupied molecular orbital (LUMO) to form a short-lived molecular radical anion (M^{•-}) as illustrated in **Equation 3.4**. The formation of M^{•-} is a second-order reaction.



If there is enough internal energy the molecular radical anion, M^{•-} may fragment to give fragment anion, X⁻ and uncharged radical species, N[•] via first-order kinetics as shown in **Equation 3.5**.



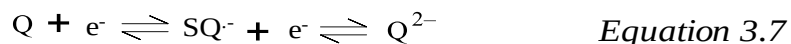
However, in the presence of a reagent gas (CH₄), the excited molecular radical anion (M^{•-}) loses its excess internal energy to form an even more stabilized molecular anion (M⁻) by second order kinetics as indicated in **Equation 3.6**. Here, CH₄ act to collisionally stabilize M^{•-} formed through resonance.



3.1.2 Cyclic voltammetry

One of the most important characteristic of quinones is their ability to undergo reversible redox reaction via a two electron process [60]. Redox potential shows the tendency of a molecule to accept or donate electrons thereby constituting the principal parameter towards understanding electron-transfer mechanisms of

quinone compounds. In aqueous buffer (acidic, neutral, or basic media) quinones (Q) undergo reversible two electron reduction while in neutral aprotic media, quinones undergo first one-electron reduction step to produce the semi-quinone ($\text{SQ}^{\bullet -}$) radical anion, followed by a second one-electron reduction process that yields the dianion quinone (Q^{2-}) as illustrated on **Equation 3.7** [19], [61].



The half wave reduction potentials of PBQ derivatives are determined by cyclic voltammetry. Voltammetric measurements are carried out in an electrochemical cell comprising of three electrodes. A schematic of a voltammetric typical setup is shown in **Figure 3.1**. The electrode labelled 1 is the working electrode, where redox processes takes place. It is normally made of platinum/gold/silver/glassy carbon. Electrode 2 in the same figure is the counter electrode, which usually serves to conduct electricity from the source to other electrodes through the electrolyte. The final electrode, 3 is the reference electrode which serves to calibrate the applied potential. Examples of reference electrodes normally used include hydrogen, silver/silver chloride (Ag/AgCl) and the saturated calomel ($\text{Hg}/\text{Hg}_2\text{Cl}_2$).

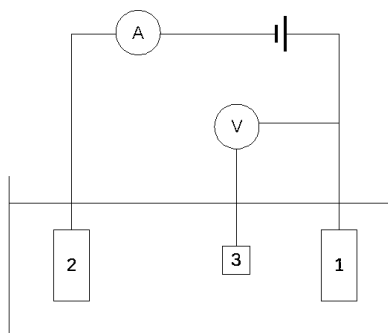


Figure 3.1: An electrochemical cell. 'V' denotes voltmeter and 'A' measures the current between the working and the counter electrodes. *Adapted from* [62].

When voltage is applied at the working electrode, current increases, and reduction of PBQ occurs. In **Figure 3.2**, the reduction process occurs when the potential is scanned negatively. The resulting current is called cathodic current (I_c), and the resultant peak potential is called the cathodic peak potential (E_c). As the voltage is increased, maximum flow of electrons will be observed until the current associated with the reduction decrease due to depletion of PBQ molecules at the working

electrode. A decrease in voltage will cause reverse oxidation process to occur, and the potential will scan positively. The resulting current is called anodic current (I_a), and its corresponding peak potential is anodic peak potential (E_a). At this stage the molecules return to their original state [63].

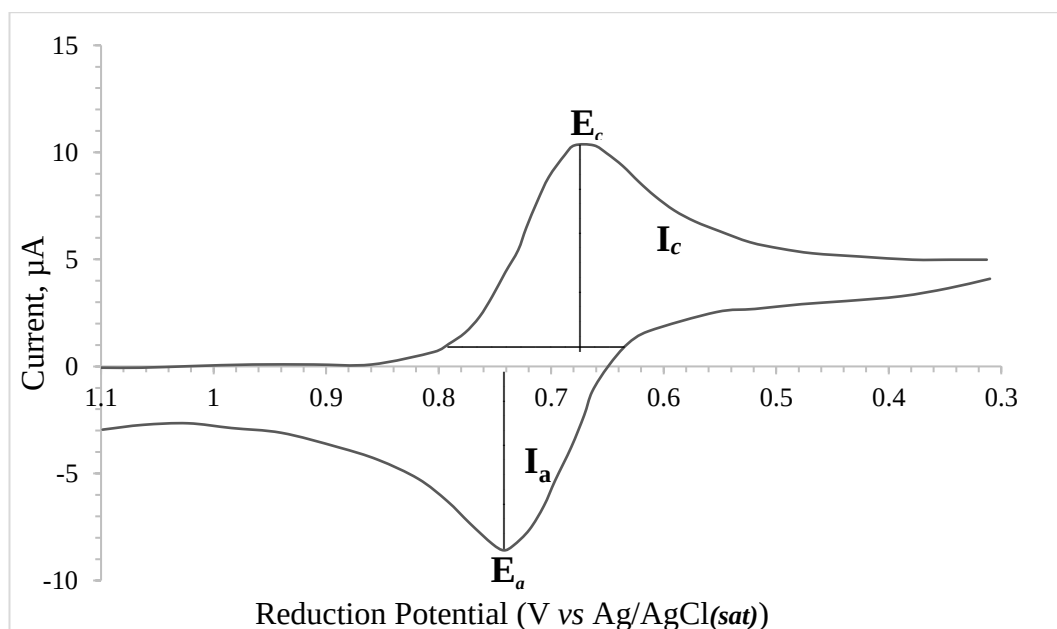


Figure 3.2: Cyclic voltammogram for a reversible one-electron redox process. Adapted from [63].

3.1.3 Theoretical estimation of the electron affinity

To understand the possible channels of dissociation of negative ions and their stability it is ideal to calculate their electron affinity [51]. Electron affinity is, essentially the opposite of the ionisation energy, instead of removing an electron from the molecule an electron is attached to the molecule to form an anion, as given in **Equation 3.8**. As shown, it is the energy difference between the lowest energy state of the neutral molecule and the lowest energy state of the corresponding negative ion [48].



Koopmans' theorem can also be used to determine the electron affinity, EA [51]. According to Koopmans' theorem, an electron is attached to the lowest unoccupied Molecular Orbital (LUMO), the energy (ϵ_{LUMO}) required to attach an electron into

the LUMO will be negative and this energy will be closely equivalent to the EA of the molecule [51]. **Equation 3.9** summarises the Koopmans' Theorem:

$$EA = -\varepsilon_{\text{(LUMO)}} \quad \text{Equation 3.9}$$

With regard to theoretical calculations, two types of EA, adiabatic electron affinity (EA_a) and vertical electron affinity (EA_v) have been discussed [49], [64]. EA_a is the energy difference between the ground state of the neutral species and the ground state of the anion, at their respective optimized geometries (**Equation 3.10**). while EA_v is the energy difference between the ground state of the neutral at its optimized geometry and the corresponding anion at the optimized geometry of the neutral molecule (**Equation 3.11**) [49], [64]. In **Equation 3.10** and **Equation 3.11**, $E_{(M)}$ is the total energy of the optimized neutral molecule, $E_{(M)}^-$ is the energy of anion state at the corresponding geometry of the neutral and $E_{(M^-)}^-$ is the total energy of the optimized anion species.

$$EA_a = E_{(M)} - E_{(M^-)}^- \quad \text{Equation 3.10}$$

$$EA_v = E_{(M)} - E_{(M)}^- \quad \text{Equation 3.11}$$

3.2 Materials, Methods and Experimental Procedures

3.2.1 Chemicals used

All the chemicals were purchased from Sigma-Aldrich Company, South Africa and they were of analytical reagent grade hence used without further purification. Ten p-benzoquinones were investigated, namely: p-benzoquinone (PBQ); 2-methyl-p-benzoquinone; 2,5-dimethyl-p-benzoquinone; tetramethyl-p-benzoquinone (duroquinone); 2-tert-butyl-p-benzoquinone; 2,6-dimethoxy-p-benzoquinone; 2,6-dichloro-p-benzoquinone; 2,5-dichloro-p-benzoquinone; 2-chloro-p-benzoquinone and tetrafluoro-p-benzoquinone. Dichloromethane (for GC-MS experiments) and acetonitrile (for cyclic voltammetry experiments) were used as solvents. 0.1M of tetraethyl ammonium tetrafluoroborate was used as a supporting electrolyte in all cyclic voltammetric experiments.

3.2.2 Gas chromatography-mass spectrometry (GC-MS)

The mass spectra were obtained on an Agilent 5975C MSD series mass spectrometer coupled to an Agilent 7890A GC system with HP-5MS 5% phenyl methyl silox capillary column (30m X 250 μ X 0.25 μ m). The electron impact ionisation mass spectra (EI-MS) were acquired at 70eV from m/z 50-200. In order to acquire mass spectra in the electron capture negative chemical ionization (ECNCI) mode, the instrument was calibrated and tuned in the EI mode as recommended by the manufacturer and then switched to NCI mode. The source and analyzer temperatures were optimized and held at 230 and 150°C respectively, throughout. In the EI mode, the electron multiplier voltage and the filament emission current were auto set to 1700V and 34.6 μ A respectively. All other parameters were also auto set by the instruments autotune function using perfluorotributylamine (PFTA) as the tune/calibration reagent. After acquiring EI spectra, the instrument was then changed to NCI mode using perfluoro-5,8-dimethyl-3,6,9-trioxidodecane (PFDTD) calibrant to adjust the mass axis using ions at 448. Methane was used as the reagent gas at a flow rate of 0.4mL/min. The GC effluent was introduced into the mass analyzer via the interface into the mass spectrometer source pressurized with the reagent gas. The ECNCI autotune function was used to set all other parameters for optimum production of thermalized electrons. The GC oven temperature was held at 50°C for 1.5 minutes then ramped to a final temperature of 300°C at 15°C/min for a total run time of 17 minutes. 5ppm solutions of each PBQ sample were injected in the splitless mode, and the injector temperature was set at 250°C. Helium .0 in the splitless mode, and the injector temperature was set at 250°C. Helium (He) gas was used as the carrier gas throughout. Before the ECNCI mass spectra of PBQ molecules were obtained, the electron ionization (EI) mass spectra were first obtained to verify the purity of all the samples under study. The EI mass spectra were recorded for all samples and then compared with spectra from the literature [65]. For ECNCI-MS, an internal standard (duroquinone) at a concentration of 3ppm was added to all the 5ppm solutions of PBQs to normalize the results. The following steps were taken to prepare 5ppm solutions injected in GC-MS;

- Approximately 0.01g of PBQ samples were dissolved in a 10.00ml dichloromethane to prepare a 100ppm stock solution.

- 0.5ml of the stock solution was then diluted with dichloromethane in a 10.00ml volumetric flask to make a 5ppm solution.

3.2.3 Cyclic voltammetry

Electrochemistry measurements were performed at room temperature using potentiostat/Galvano stat/ ZRA: Gamry instrument reference 600+ controlled by a computer system through potentiostat control software program “Gamry Instruments Framework”. The working electrode used was a hanging mercury drop electrode, while a platinum wire counter-electrode and a non-aqueous Ag/AgCl_(sat) reference electrode (Gamry instrument reference 600+) were used for all the measurements. 0.1M tetraethyl ammonium tetrafluoroborate in acetonitrile was used as a supporting electrolyte. 2mM samples of the PBQs were used. The cyclic voltammetry parameters were set as follows: initial potential; 0.2V, final potential; 0.2V, number of cycles; 2, scan rate; 100mV/s and full scale (+/-); 0.1A. The voltammograms for all the molecules analyzed were obtained and reduction potentials were calculated using *Equation 3.12*.

$$E = \frac{E_c + E_a}{2} \quad \text{Equation 3.12}$$

E_c and E_a are reduction potentials obtained approximately at half-height of the cathodic and anodic peaks respectively while E is the average reduction potential of E_c and E_a . At these points the concentration of the reduced and oxidized species were expected to be equal [66].

3.2.4 Computational methods

The calculations presented in this work were carried out on a Dell, Latitude E6440 computer with Intel Core i5, 8.00GB RAM and 64-bit operating system. GAUSSIAN 03 program software was used to calculate geometrical parameters, electron affinities and vibrational frequencies of all the compounds under study. Density functional theory using Becke's three-parameter exchange combined with the correlation functional of Lee, Yang and Parr (B3LYP) [48], [67] and the 6-

311G++(d,p) basis set were used. Geometry optimizations and frequency calculations were performed for the neutral, and anionic states of each molecule in their ground electronic state. From the calculations, the adiabatic and vertical electron affinities were calculated using **Equation 3.10** and **Equation 3.11** respectively. Bond lengths and bond angles were extracted from the optimized structures of PBQ, and its derivatives and these values were compared to the literature. Vibrational frequencies were also obtained at the same level of theory and were used to characterize the stationary points as minima.

Theoretical mass spectra were calculated using the QCEIMS program [68]. We used the extended tight binding method (GFN-xTB) which focuses on reproducing properties near the minimum in the potential energy surface such as vibrational frequencies and geometries. In this method the dispersion interaction is treated using Grimme's D3 correction [69], [70]. The program was run on the dissociative electron attachment mode with electron impact energies ranging from 0 to 15eV, with a step size of 0.05eV. For each initial configuration of the benzoquinone, Born–Oppenheimer *ab initio* molecular dynamics (BOMD) is initiated. Here classical trajectories of the nuclei are calculated based on the quantum mechanically calculated forces. The dynamics are terminated based on the number of steps, number of fragments produced or when the maximum molecular dynamic time for a given trajectory track has been reached. There were 300 trajectories for the production run of each PBQ molecule and each trajectory had 20 000 steps. The step size of each molecular dynamics step was set to 0.5fs, giving the maximum molecular dynamic time for a given trajectory 10ps to complete. If fragmentation occurs, the statistical charges and the electron affinities of each fragment calculated were used to determine which fragment carries a charge. The sum of the statistical charges for all fragments is always -1. The fragment with the highest electron affinity and charge value carried the -1 charge and it was observed in the mass spectrum while the one with lower charge value was considered the uncharged free radical which does not show on the mass spectrum since it does not bear a charge. Furthermore, the sum of the statistical charges of a particular fragment, over the entire set of production runs, produces the relative intensity of that fragment.

4 RESULTS AND DISCUSSION

The main purpose of this chapter is to present, analyse and interpret data obtained in this study. The chapter is structured as follows: in section 4.1, analysis of the results obtained via electron impact ionisation (EI) are shown to mainly verify the purity of samples. Then section 4.2 present a description on the electron capture negative chemical ionisation mass spectrometry (ECNCIMS), QCEIMS (negative in mode) mass spectra and possible fragmentation pathways of PBQs. Moreover, there will be concluding remarks on ECNCIMS in this section. Lastly section 4.3, will present and discuss the information obtained on the molecular properties of PBQs such as reduction potentials, electron affinities, geometrical potentials, and C=O vibrational frequencies of PBQs. Additionally, the experimental and theoretical spectra will be compared while correlating the electron affinities with reduction potentials and molecular anion signal responses (stability). In all sections, the effects of electron donating substituents and electron withdrawing substituents will be discussed.

4.1 Electron Impact Ionisation Mass Spectra (EI-MS)

The results obtained (**Table 4.1** and **Table 4.2**) agrees well with the previous data from NIST [65]. This appropriate reproducibility validate a successful tuning and calibration of GC-MS instrument into EI mode which is a requirement before switching to ECNCI mode in addition to verifying the purity of the samples used.

4.1.1 Effects of electron donating substituents on PBQ⁺

Table 4.1 and **Figure 4.1** show the EIMS analysis of PBQ and its electron donating derivatives under this study. Methylated PBQs show the same fragmentation pattern which involves elimination of either CO and/or C₂H₂. EIMS spectra of electron donating derivatives of PBQ of the same compounds have shown the same fragmentation pattern observed previously [65]. The molecular ion peaks do not form the base peaks in most compounds except for 2,5-dimethyl PBQ.

Table 4.1: Main peaks in the EI-mass spectra of PBQs with electron donating substituents.

Compound	Cation fragment	m/z ratio	Relative intensity (%)
PBQ	$[M]^+$	108	55
	$[M-C_2H_2]^+$	82	24
	$[M-CO]^+$	80	18
	$[M-(CO+C_2H_2)]^+$	54	100
	$[M-(2CO)]^+$	52	25
2-methyl PBQ	$[M]^+$	122	87
	$[M-CO]^+$	94	100
	$[M-(C_2CH_3)]^+$	82	59
	$[M-(2CO)]^+$	66	59
	$[M-(CO+C_2CH_3)]^+$	54	77
2,5-dimethyl PBQ	$[M]^+$	136	100
	$[M-CO]^+$	108	37
	$[M-(C_2CH_3)]^+$	96	18
	$[M-(2CO)+H]^+$	79	45
	$[M-(CO+C_2CH_3)]^+$	68	63
Duroquinone	$[M]^+$	164	60
	$[M-(CO)]^+$	136	53
	$[M-(CO+CH_3)]^+$	121	100
	$[M-(2CO+CH_3)]^+$	93	35
	$[M-(CO+2CH_3+2CH_2+C_2)]^+$	54	17
2-tert-butyl PBQ	$[M]^+$	164	29
	$[M-(CH_3)]^+$	149	100
	$[M-(CO+CH_3)]^+$	121	87
	$[M-(C(CH_3)_3+CH)]^+$	94	38
	$[M-(2CO+CH_3)]^+$	93	42
	$[M-(CO+(CH_3)_3)]^+$	91	52
	$[M-(CO+C_2HC(CH_3)_3)]^+$	54	39
2,6-dimethoxy PBQ	$[M]^+$	168	23
	$[M-(2CO+CH_3)]^+$	97	18
	$[M-(CO+OCH_3+CH_3+C_2H)]^+$	69	100

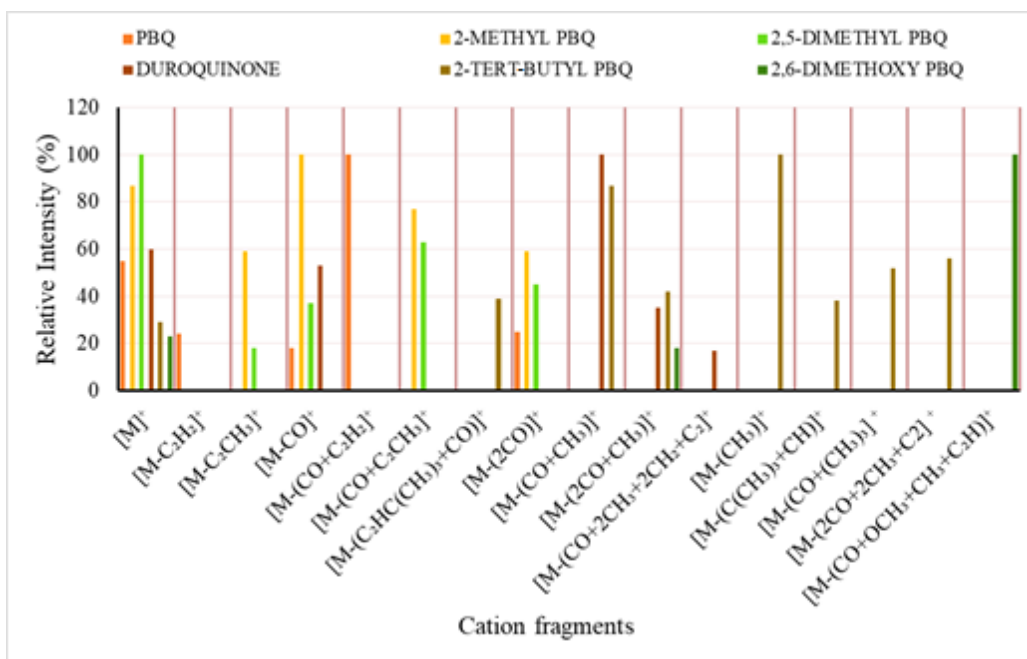
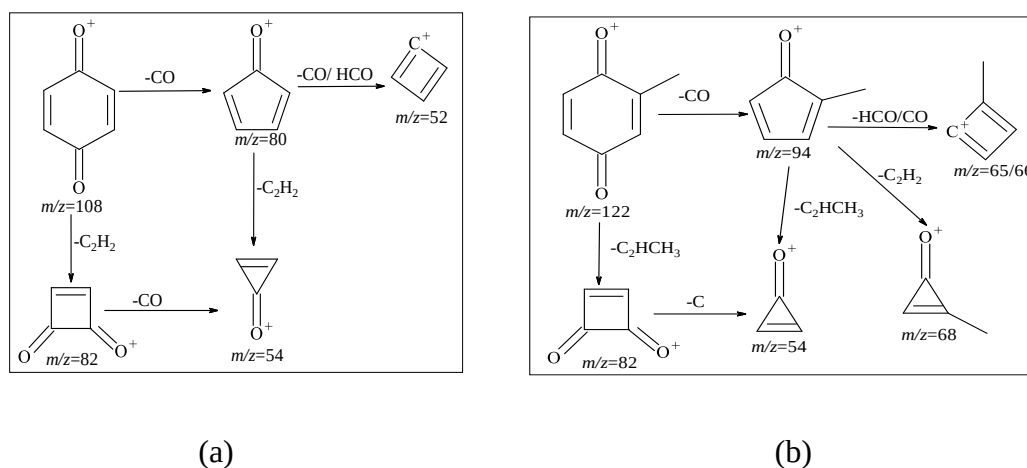
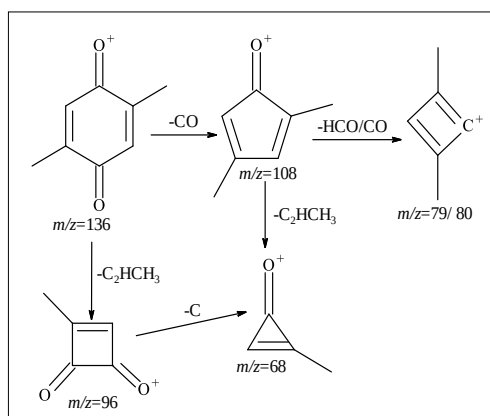


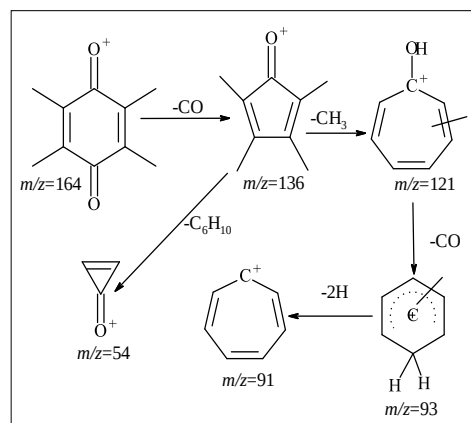
Figure 4.1: Main peaks in the EI-mass spectra of PBQs with electron donating substituents.

It is known that PBQ derivatives containing methyl group substituents show common fragmentation pathways similar to that of PBQ as illustrated in **Scheme 4.1** [71]. However, the relative intensities for the same fragment ions differ across these compounds. This is a pointer to the differences in the relative stabilities of the parent molecules.

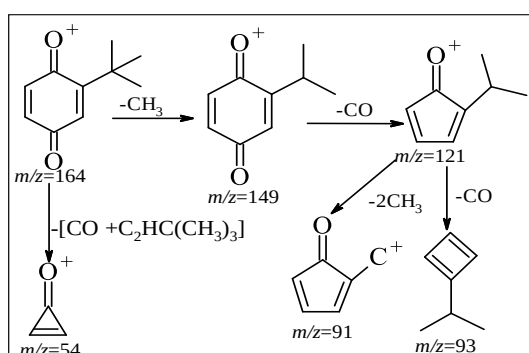




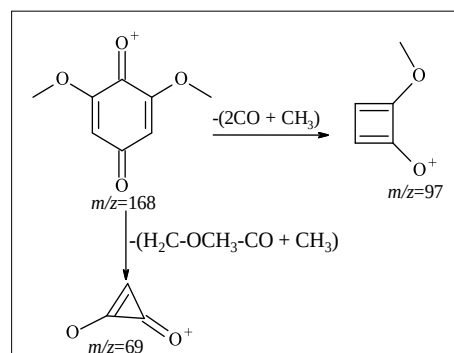
(c)



(d)



(e)



(f)

Scheme 4.1: Plausible fragmentation pathways of (a) PBQ *adapted from* [60], [71] (b) 2-methyl PBQ *adapted from* [71], (c) 2,5-dimethyl PBQ *adapted from* [71], (d) duroquinone *adapted from* [71], (e) 2-tert-butyl PBQ, and (f) 2,6-dimethoxy PBQ.

During dissociation, the molecular ion either expels CO or acetylene to form $[M-CO]^+$ or $[M-acetylene]^+$ respectively [60]. The observed ion fragments arising from loss of CO have different peak intensities with 2-methyl PBQ having the most abundant ion fragment (100%) at m/z 94, followed by duroquinone (53%) at m/z 136, then 2,5-dimethyl PBQ (37%) at m/z 108, and PBQ which produced the weakest peak (18%) at m/z 80. The intensities of the $[M-acetylene]^+$ peak for the asymmetrical substituted PBQ is enhanced relative to that of PBQ (24%). For example, 2-methyl PBQ showed increased relative intensity of $[M-acetylene]^+$ to 59% at m/z 82 compared to 18% obtained at m/z 96 in 2,5-dimethyl PBQ [60], [71]. Duroquinone and 2-tert-butyl PBQ showed very strong peaks at m/z 121 corresponding to loss of CO accompanied by elimination of CH_3 . As for duroquinone the ring was forced to expand to form a more favourable stable

carbonium ion with a 100% relative intensity. This has been reported before by Bowie *et al* [71]. The prominent loss of CO and acetylene in all electron donating derivatives of PBQ were also observed. These observations have also been observed by Gross [60] and Beynon *et al* [72]. The availability of a methyl group in the molecule makes it easier for CO to detach because methyl group substituents are good activators and ortho-para directors. This leads to activation and elimination of CO in the para-position of the quinone molecules. The position of a methyl substituent also plays a vital role on the intensity of the fragment ion formed. For example, between 2,3-dimethyl PBQ and 2,5-dimethyl PBQ a very strong peak (80%) was expected at m/z 54 in 2,3-dimethyl PBQ because the most substituted ethylene group is expected to be eliminated unlike in 2,5-dimethyl where the methyl groups are symmetrically substituted hence giving a peak (63%) at m/z 68 [60], [72].

Another common fragment ion observed in the mass spectra of these compounds was due to loss acetylene or the most substituted acetylene followed by elimination of CO to form the cyclopropenone cation. This cation was observed at m/z 54 in PBQ (100%) and 77% in 2-methyl PBQ whereas in duroquinone and 2-tert-butyl PBQ, it was formed with very low peak intensities of 17% and 39% respectively. Substituted cyclopropenone fragments, following the same fragmentation pathways were observed for 2,5-dimethyl PBQ and 2,6-dimethoxy PBQ at m/z 68 and 69, respectively. Notice that for 2-methyl PBQ following the same pathway, when the most substituted ethylene was substituted, a cyclopropane was formed but if an unsubstituted acetylene was eliminated, a substituted cyclopropane was formed with relatively the same intensities. Furthermore, there is a characteristic feature which is significantly visible in **Figure 4.1** and **Table 4.1**, resulting from loss of 2CO to form ionized cyclobutadiene and cyclohexatriene. 2,5-dimethyl PBQ and duroquinone, first eliminated CO to form ions at m/z 108 and 136 respectively. This was then followed by consecutive loss of H/CH₃ and the second CO to form cyclobutadiene and cyclohexatriene respectively [71], [73]. 2-tert-butyl PBQ formed a much-stabilised ion fragment at m/z 149 due to loss of one methyl group from the tert-butyl substituent.

4.1.2 Effects of Electron Withdrawing Substituents on PBQ+

Electron withdrawing groups of PBQ were also studied using GC-EI-MS. Their m/z and the relative intensities are shown in **Table 4.2** and Error! Reference source not found.. The molecular cations did not form base peaks in the mass spectra. However, the tetrafluoro PBQ⁺ which has a stabilizing effect on PBQ⁺ signal was quite strong (97%).

Table 4.2: Main peaks in the EI-mass spectra of PBQs with electron withdrawing substituents.

Molecule	Cation	m/z ratio	Relative Intensity (%)
PBQ	$[M]^+$	108	55
	$[M-C_2H_2]^+$	82	24
	$[M-CO]^+$	80	18
	$[M-(CO+C_2H_2)]^+$	54	100
	$[M-(2CO)]^+$	52	25
2-chloro PBQ	$[M]^+$	142	49
	$[M-(2CO+C_2H_2)]^+$	60	100
	$[M-(2CO)]^+$	86	16
	$[M-(CO+C_2HCl)]^+$	54	49
	$[M-(C_2H_2)]^+$	116	9
2,5-dichloro PBQ	$[M]^+$	176	30
	$[M-(2CO+C_2HCl)]^+$	60	100
	$[M-(CO+C_2HCl)]^+$	88	29
	$[M-(2Cl+CO+C_2)]^+$	53	52
	$[M-(2CO)]^+$	120	10
2,6-dichloro PBQ	$[M]^+$	176	55
	$[M-(2CO+C_2HCl)]^+$	60	100
	$[M-(CO+C_2HCl)]^+$	88	47
	$[M-(2Cl+CO+C_2)]^+$	53	61
	$[M-(2CO)]^+$	120	23
Tetrafluoro PBQ	$[M]^+$	180	97
	$[M-(2CO+C_2F_2)]^+$	62	78
	$[M-(2CO)]^+$	124	100
	$[M-(2CO+CF)]^+$	93	26
	$[M-(CO+C_2F_2)]^+$	90	18
	$[M-(C_2F_2+CO+F)]^+$	71	53

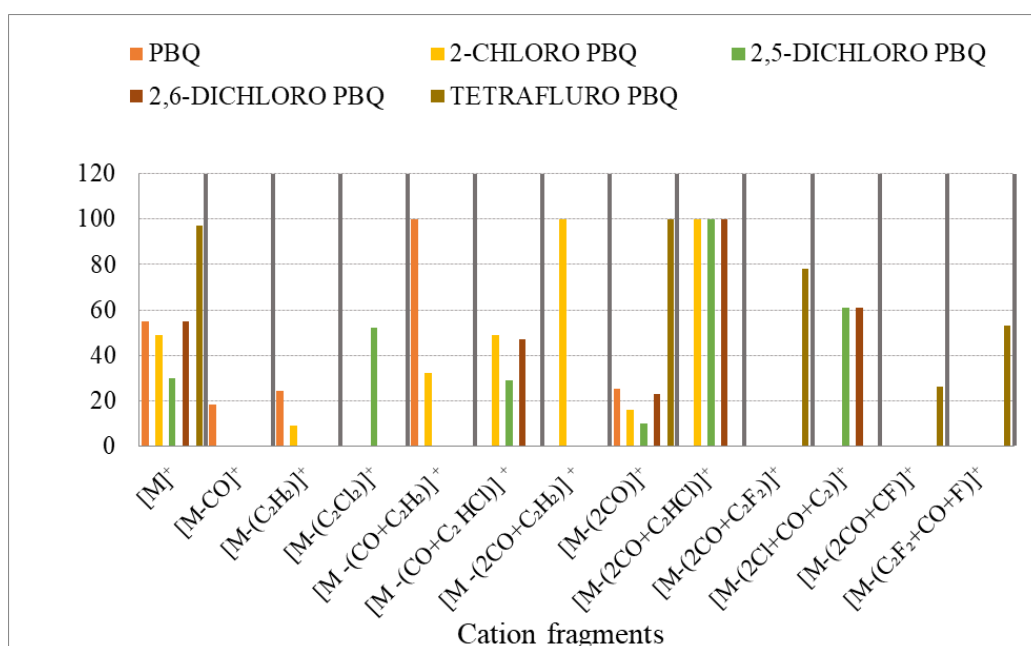
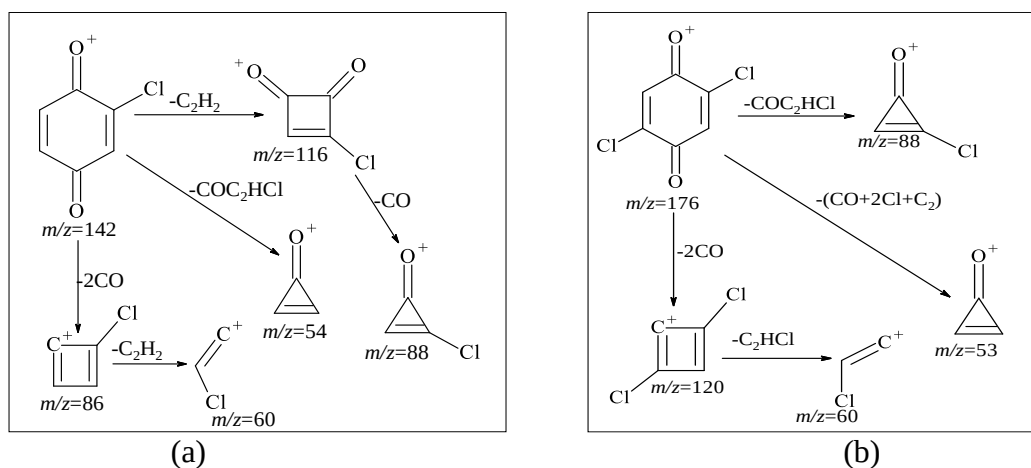
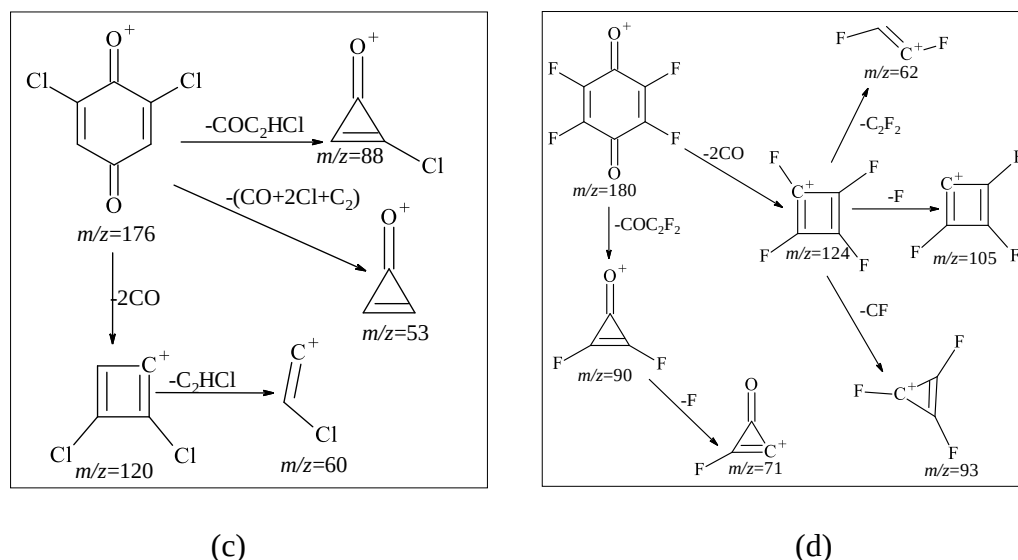


Figure 4.2: Main peaks in the EI-mass spectra of PBQs with electron withdrawing substituents.

Scheme 4.2 illustrates the fragmentation pathways that resulted in the formation of ion fragments presented in **Table 4.2** and **Figure 4.2**. It became evident that there was no $[M-CO]^+$ with electron withdrawing groups as was observed with electron donating groups. Elimination of acetylene to form $[M-C_2HX]^+$ ($X=Cl, F$) was also uncommon, as it was only observed in 2-chloro PBQ at m/z 116 at a very low intensity. The most common fragments were $[M-2CO]^+$ and $[M-(CO+C_2HX)]^+$ ($X=Cl, F$). Fragmentation by elimination of 2CO followed by loss of most substituted acetylene or vice versa tended to form stabilized fragment cations. However, in tetrafluoro PBQ the most intense cation fragment was $[M-(2CO)]^+$.





Scheme 4.2: Plausible fragmentation pathways of (a) 2-chloro PBQ, (b) 2,5-dichloro PBQ, (c) 2,6-dichloro PBQ and (d) tetrafluoro PBQ.

4.2 Electron Capture Negative Chemical Ionisation Mass Spectra (ECNCIMS)

4.2.1 ECNCIMS of methylated PBQs

The experimental and theoretical ECNCIMS spectra of PBQ are shown in **Figure 4.3**. These spectra comprised of different types of anions, one of which represented the molecular anion (M^-) which had 100% intensity i.e., the base peak of the spectra. The theoretical spectrum also showed intense peaks at m/z 41, 53, 54, 55, 80, 81, 106 and 107 while the experimental spectrum had only four peaks at m/z 80, 92, 106 and 107. In addition to the four peaks produced in the experimental spectrum, there were peaks which corresponded to anions with m/z ratios that were higher than that of the molecular anion (m/z 109, 110, 111, 120, 122, 123, 124, 125, 127, 136 and 138) the peak at m/z 109 is an isotopic peak and also occurs in the theoretical spectrum. The peaks at m/z 80, 106 and 107 appeared in both the experimental and the theoretical spectra.

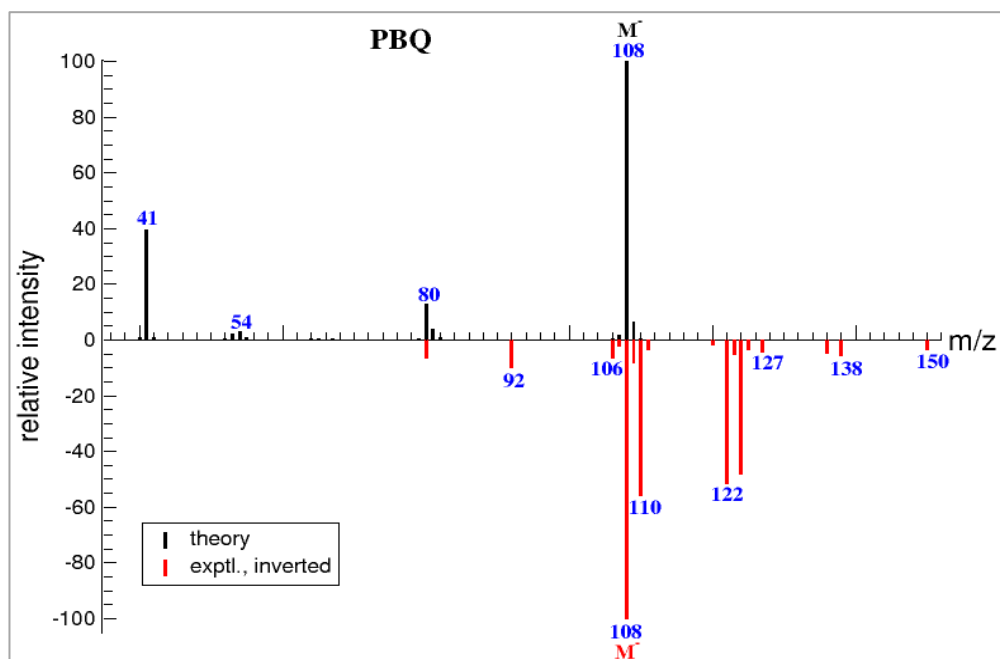


Figure 4.3: The theoretical and experimental mass spectra of PBQ

The mass spectra of methylated PBQs are also reported in **Figure 4.4-Figure 4.7**. The spectra retained several features of the spectra of PBQ. They had pronounced molecular anion peaks. Similar to PBQ, there were five prominent peaks at m/z 41, 53, 54, 55, 80 and 81 (**Figure 4.4, Figure 4.5 and Figure 4.7**). To the contrary, the spectra of duroquinone in **Figure 4.6** showed fewer peaks at m/z 136, 149 and 163. Not only three peaks are observed in the theoretical spectrum of duroquinone, but also a peak at m/z 55 was present. There was a significant peak at m/z 41 in almost all theoretical spectra of PBQs under study, which was absent in the experimental spectra. The mass spectra were acquired from m/z 50 – 200 and this mass scan range did not bracket all the mass for the fragment anion with m/z 41, hence its absence in the experimental spectra.

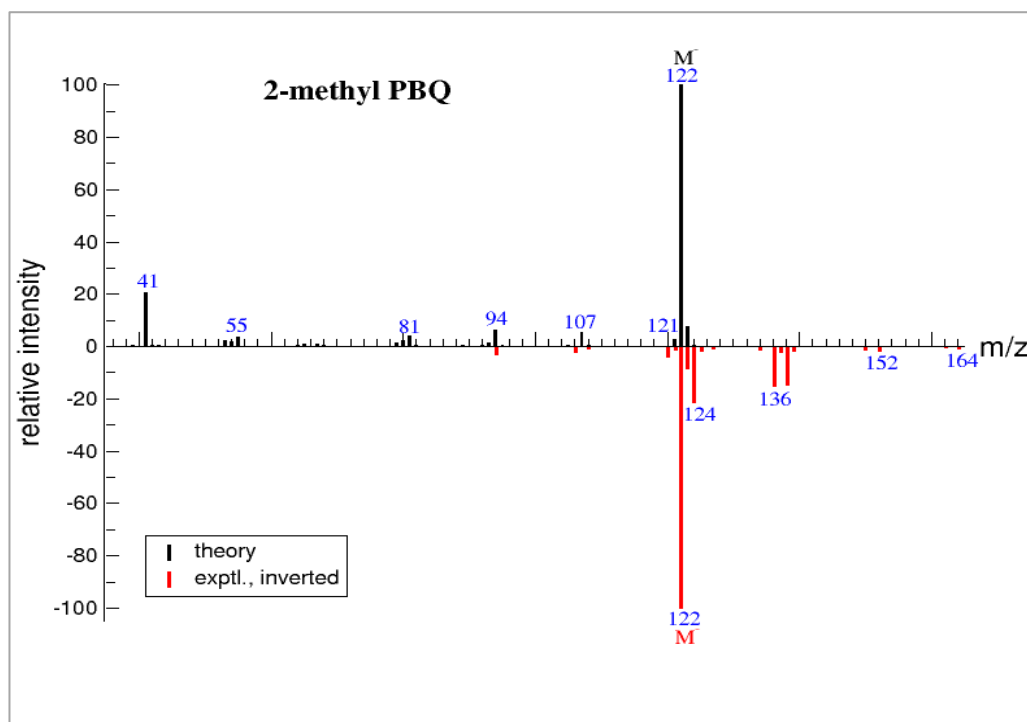


Figure 4.4: The theoretical and experimental mass spectra of 2-methyl PBQ

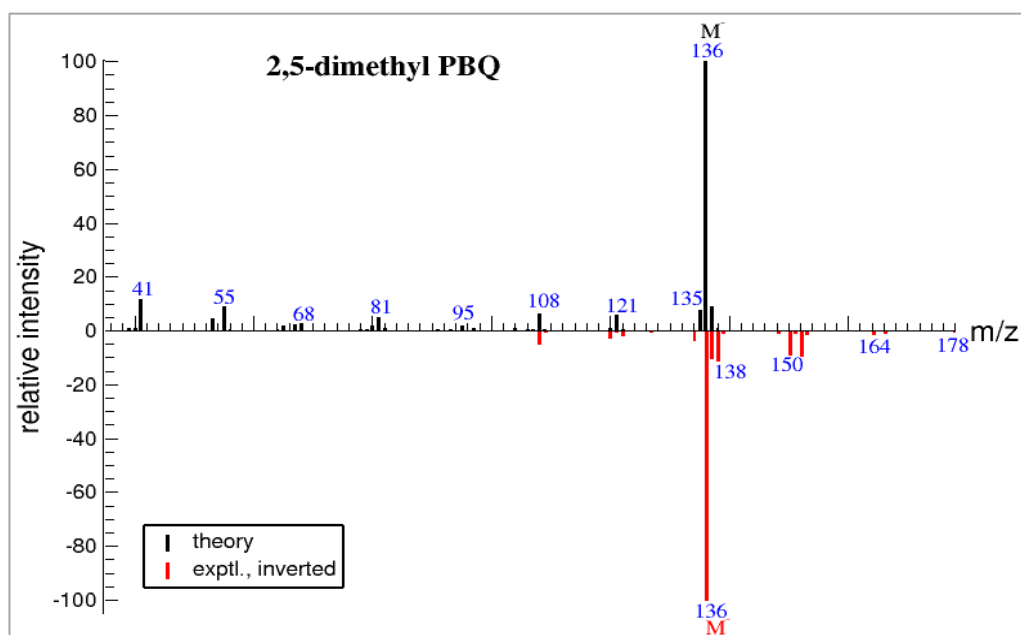


Figure 4.5: The theoretical and experimental mass spectra of 2,5-dimethyl PBQ

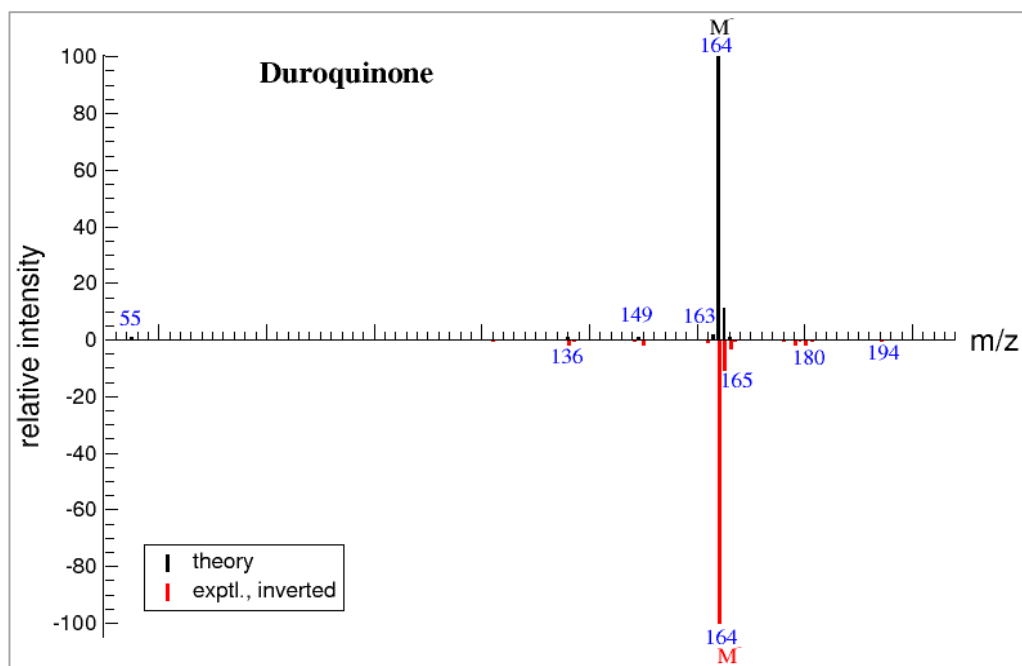


Figure 4.6: The theoretical and experimental mass spectra of duroquinone

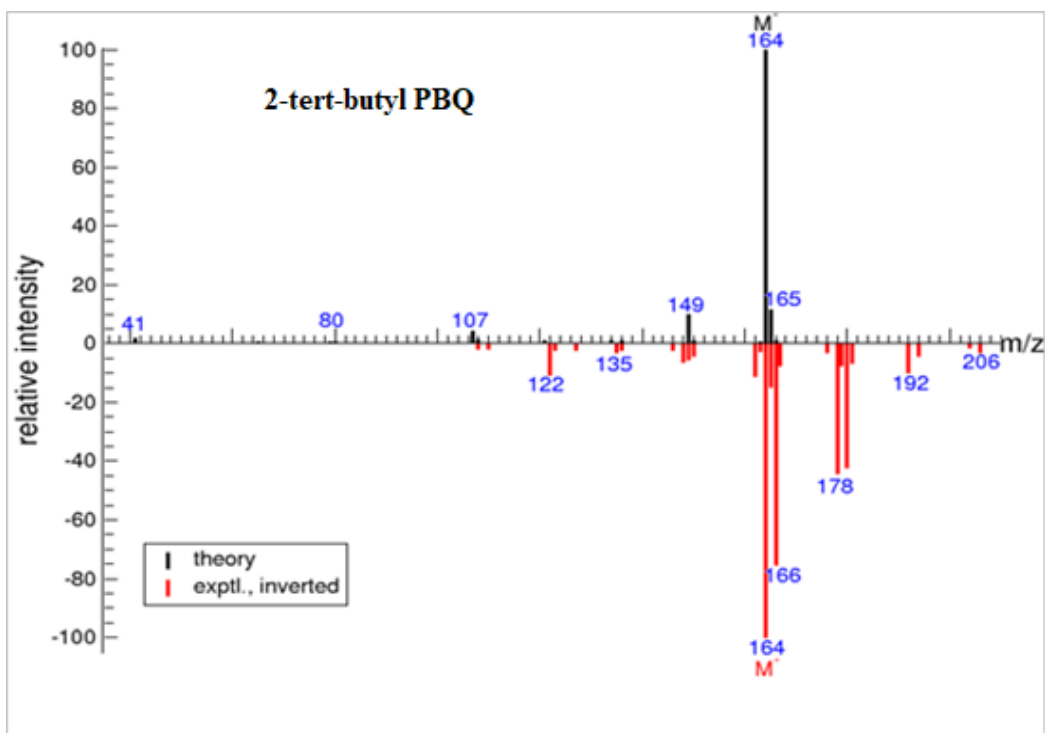
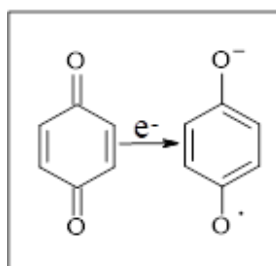


Figure 4.7: The theoretical and experimental mass spectra of 2-tert-butyl PBQ

The most intense peaks in the mass spectra of PBQs in **Figure 4.4-Figure 4.7** corresponded to the formation of a well stabilized, long-lived molecular anion, M^- . Due to the availability of the π -system, PBQs form resonance stabilized molecular anions by electron capture [74], [75]. The additional electron enters the lowest

unoccupied molecular orbital (LUMO) of PBQs which is characterised by π^* -orbital and this brings an extra stability to the system [54] as seen in **Scheme 4.3**. The lower the energy of the LUMO, the higher is the expected electron affinity. When the extra electron is in the π^* LUMO, the negative charge is mostly situated on the two oxygen's. According to Heinis et al [75], due to large positive electron affinity, PBQ forms a stable molecular anion. This stability reduces when electron donating substituents are added to PBQ and increases with addition of electron withdrawing substituents.



Scheme 4.3: Resonance electron capture of PBQ molecule. *Adapted from* [54]

The theoretical mass spectra showed more peaks compared to experimental mass spectra. This could have been due to the insensitivity of mass spectrometer or the inadequacy of the theoretical method to describe the system. ECNCIMS is strongly affected by experimental conditions. When a low accelerating voltage is used, the detection of negative ions at the secondary electron multiplier (SEM) becomes a problem. A high negative entrance potential of SEM on the first dynode will cause strong obstruction of the ion beam. This leads to loss of sensitivity of detection by the mass spectrometer [58]. Another observation noted in experimental spectra, was the availability of peaks of anions with higher m/z values, (i.e., higher than the molecular ion) shown in **Table 4.3**. These peaks were not available in the theoretical mass spectra due to the inability of computational methods used to calculate m/z higher than that of the molecular anion unless it was an isotopic peak. These peaks resulted from the attachment of alkyl radicals/ion species present in methane gas, and traces of impurities, (mainly H_2O and O_2 and their reaction products with the methane gas) which reacted with PBQ molecules to give adducts of the type $[\text{M}+\text{C}_n\text{H}_{2n+1}]^-$, $[\text{M}+\text{C}_n\text{H}_{2n}]^-$, $[\text{M}+\text{O}]^-$, and $[\text{M}+\text{OH}]^-$ species [76], [77]. The alkyl radical/ ion species observed in this study include H_2 , CH_2 , CH_3 , C_2H_5 , C_2H_4 , $[\text{H} + \text{C}_2\text{H}_5]$ and C_3H_6 . An ideal reagent gas is expected to produce thermal electrons with a well-defined energy distribution close to 0 eV and it should not

interfere with the ionization process nor react with PBQ molecules. None of the reagent gases known so far, (including methane) satisfies this pre-requisite, hence the appearance of ECNCI spectra for a given compound will always change with changes in experimental parameters [76]. Increasing the pressure of methane above 1.3 Pa, when the ion source pressure is 65 Pa, initiates ion/molecule reactions between primary methane ions and neutral methane molecules forming alkyl radical species which react predominantly by proton/ hydride transfer reactions with PBQ molecules before ionization [77]–[79].

Table 4.3: Peaks of anions with m/z values higher than the molecular anion observed in experimental spectra.

Anion Fragment	m/z (Relative Intensities (%))				
	PBQ	2-methyl PBQ	2,5- dimethyl PBQ	Duroquinone	2-tert-butyl PBQ
$[M+H_2]^-$	110 (55.9)	124 (21.4)	138 (11.2)	166 (2.9)	166 (75.2)
$[M+CH_2]^-$	122 (51.7)	136 (15.3)	150 (8.8)	178 (1.7)	178 (44.1)
$[M+CH_3]^-$	123 (5.2)	137 (2.3)	151 (1.0)	179 (0.2)	179 (7.5)
$[M+O]^-$	124 (48.0)	138 (14.8)	152 (9.5)	180 (1.8)	180 (42.4)
$[M+OH/CH_5]^-$	125 (3.3)	139 (1.8)	153 (1.2)	181 (0.2)	181 (6.6)
$[M+C_2H_4]^-$	136 (4.9)	150 (1.3)	164 (1.2)	192 (0.2)	192 (10.0)
$[M+H+C_2H_5]^-$	138 (5.7)	152 (1.8)	166 (1.0)	194 (0.4)	194 (4.4)
$[M+C_3H_6]^-$	150 (3.4)	164 (0.9)	178 (0.5)	206 (0.1)	206 (2.9)

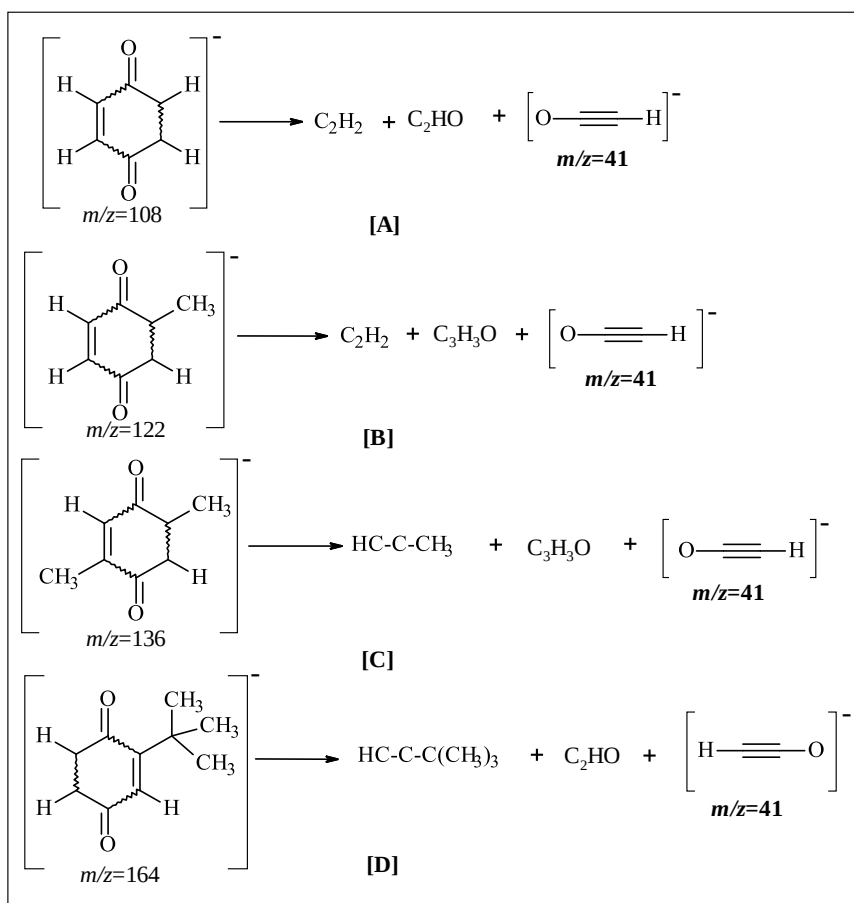
4.2.1.1 Origins of the peaks at m/z 41, 53, 54, 55, 80, 81 in the mass spectra

Table 4.4 gives a summary of most commonly occurring anionic fragments in the mass spectra of methylated PBQs. According to previous studies,[6], most of fragment anions formed were due to elimination of an ethylene (C_2H_2) from the molecular anion of PBQ, accompanied by either migration of H-atom to a nearby or distant C-atom or detachment of H-atom/s. With the aid of the calculations, the same observation was seen, and it was possible to design plausible fragmentation pathways for the formation of the above-mentioned fragment anions produced.

The peak at m/z 41 corresponded to $[C_2HO]^-$ and was only observed in the theoretical spectra. The intensity of this peak varied across these molecules. With each addition of a methyl group to PBQ, the intensity gradually decreased. The theoretically observed fragmentation pathways of the molecular anion to form $[C_2HO]^-$ is illustrated in **Scheme 4.4**. In **Scheme 4.4[A]**, the molecular anion ring opens by breaking the single bonds which allows elimination of C_2H_2 , and then the breaking of the $C=C$ bond follows which results in the formation of $[C_2HO]^-$ and C_2HO radical molecule. Similarly, the theoretical fragmentation pathways in **Scheme 4.4[B-D]** showed the formation of $[C_2HO]^-$ but there were slight differences observed. For 2-methyl PBQ and 2,5-dimethyl PBQ, **Scheme 4.4[B]-[C]**, in addition to acetylene, ($C_2H_2/ HC-C-CH_3$) and $[C_2HO]^-$, a radical species, C_3H_3O was also formed. Compared to other methyl PBQs, the formation of $[C_2HO]^-$ in 2-tert-butyl PBQ was speculated to occur via direct detachment of $[C_2HO]^-$ followed by elimination of acetylene substituted with a tert-butyl group ($-C(CH_3)_3$) (m/z 82) to produce another $[C_2HO]^-$, **Scheme 4.4[D]**.

Table 4.4: commonly occurring anion fragments in methylated PBQs observed in mass spectra. (NB: (**Bold**) experimental relative intensities).

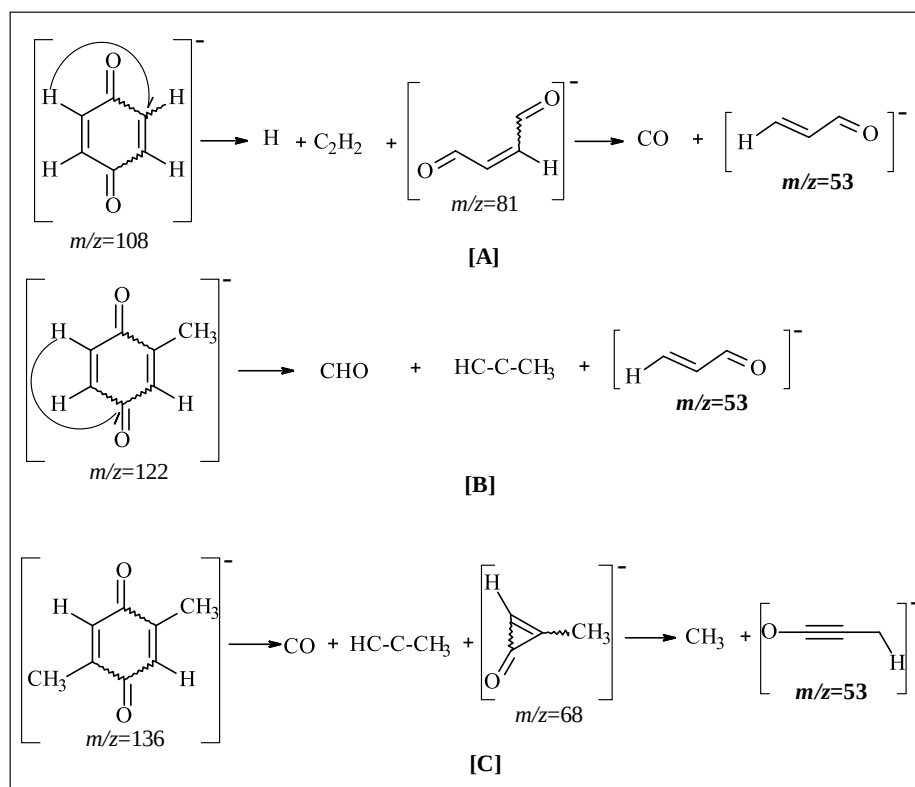
m/z	Anion fragment	Relative Intensities (%)				
		PBQ	2-methyl PBQ	2,5-dimethyl PBQ	Duro	2-ter-butyl PBQ
41	$[C_2HO]^-$	39.5	20.7	11.5	-	1.8
53	$[C_3HO]^-$	2.1	2.3	4.4	-	-
54	$[C_3H_2O]^-$	3.1	1.9	0.2	-	-
55	$[C_3H_3O]^-$	0.8	3.7	9.0	0.8	0.04
80	$[C_4O_2]^-/[C_5H_4O]^-$	12.8 (6.4)	2.3	2.0	-	0.5
81	$[C_4HO_2]^-$	3.7	4.0	5.0	-	-



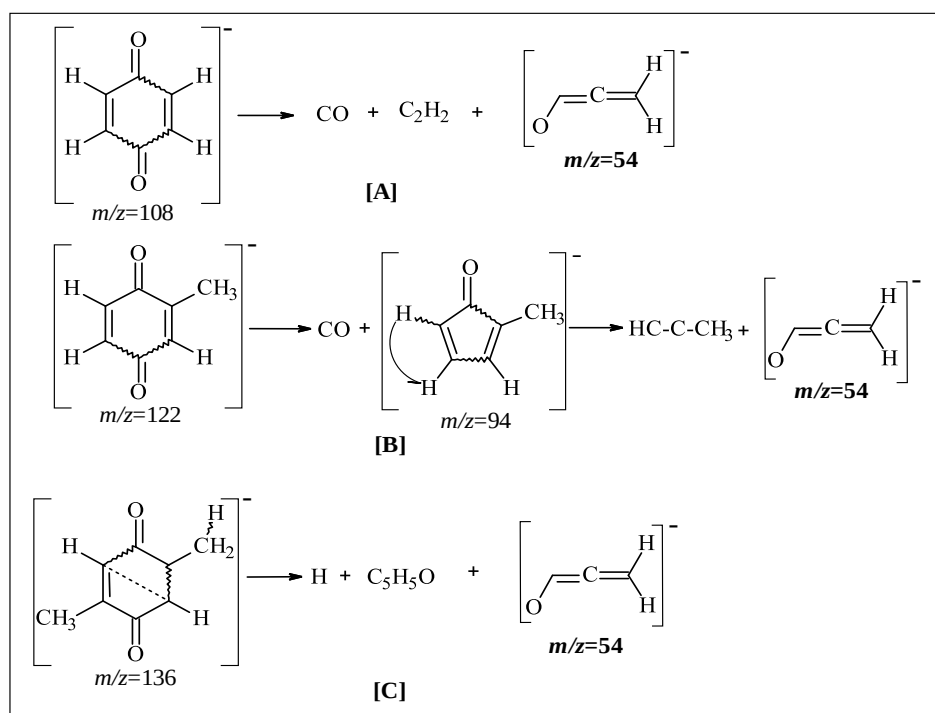
Scheme 4.4: Theoretically calculated fragmentation pathways for the formation of $[\text{C}_2\text{HO}]^-$

Another common feature in the mass spectra of methylated PBQs was the occurrence of $[\text{C}_3\text{HO}]^-$ and $[\text{C}_3\text{H}_2\text{O}]^-$ with m/z 53 and 54, respectively. The abundance of $[\text{C}_3\text{HO}]^-$ increased while that of $[\text{C}_3\text{H}_2\text{O}]^-$ decreased as the number of methyl groups attached to the ring increased (**Table 4.4**). **Scheme 4.5** and **Scheme 4.6**, illustrate the formation of $[\text{C}_3\text{HO}]^-$ and $[\text{C}_3\text{H}_2\text{O}]^-$ as a two-step process, elimination of an acetylene followed by elimination of either CO/COH or vice versa. This theoretical fragmentation pathway was very comparable to the one proposed previously [6], in which the opening of the PBQ molecular anion ring (accompanied by migration of H-atom onto a distant C-atom for the formation of $[\text{C}_3\text{HO}]^-$) is followed by elimination of acetylene (C_2H_2) and carbon monoxide (CO) resulting in the formation of $[\text{C}_3\text{HO}]^-$ (m/z 53) and $[\text{C}_3\text{H}_2\text{O}]^-$ (m/z 54). From the calculations, the breakdown of the molecular anion occurs after the elimination of H-atom producing acetylene radical and $[\text{C}_4\text{HO}_2]^-$ observed in the spectrum (**Figure 4.4**) at m/z 81. Then the dissociation of the $[\text{C}_4\text{HO}_2]^-$ into CO and $[\text{C}_3\text{HO}]^-$

occurred after migration of H-atom to a distant C-atom, (**Scheme 4.5[A]**). To obtain $[\text{C}_3\text{H}_2\text{O}]^-$ with m/z 54, the same mechanism was observed without prior elimination of H-atom and the formation of $[\text{C}_4\text{HO}_2]^-$ was absent, (**Scheme 4.6[A]**). Likewise, 2-methyl PBQ and 2,5-dimethyl PBQ showed the same mechanisms to produce anions at m/z 53 and 54 but the order at which the radicals were ejected differed. In **Scheme 4.5[B]** the molecular anion of 2-methyl PBQ fragments into $[\text{C}_3\text{HO}]^-$ (m/z 53), CHO and most substituted ethylene (HC-C-CH_3) radicals after the H-atom transferred to a distant C-atom while $[\text{C}_3\text{H}_2\text{O}]^-$ (m/z 54) was formed via the fragmentation pathway was observed as shown in **Scheme 4.6[A]-[B]**. In comparison, 2,5-dimethyl PBQ fragments by first eliminating CO, followed by ejection of most substituted ethylene (HC-C-CH_3) radicals. The elimination of two radical molecules resulted in the formation of $[\text{C}_3\text{HOCH}_3]^-$ with m/z 68 (visible in the spectrum, **Figure 4.5**). This fragment rearranged to form a stabilized three-membered ring which preferentially eliminated CH_3 and as a result the ring opened to form $[\text{C}_3\text{HO}]^-$, (**Scheme 4.5[C]**). After elimination of H-atom from the molecular anion of 2,5-dimethyl PBQ, $[\text{C}_3\text{H}_2\text{O}]^-$ (m/z 54) detach directly from the molecular anion (**Scheme 4.6[C]**).

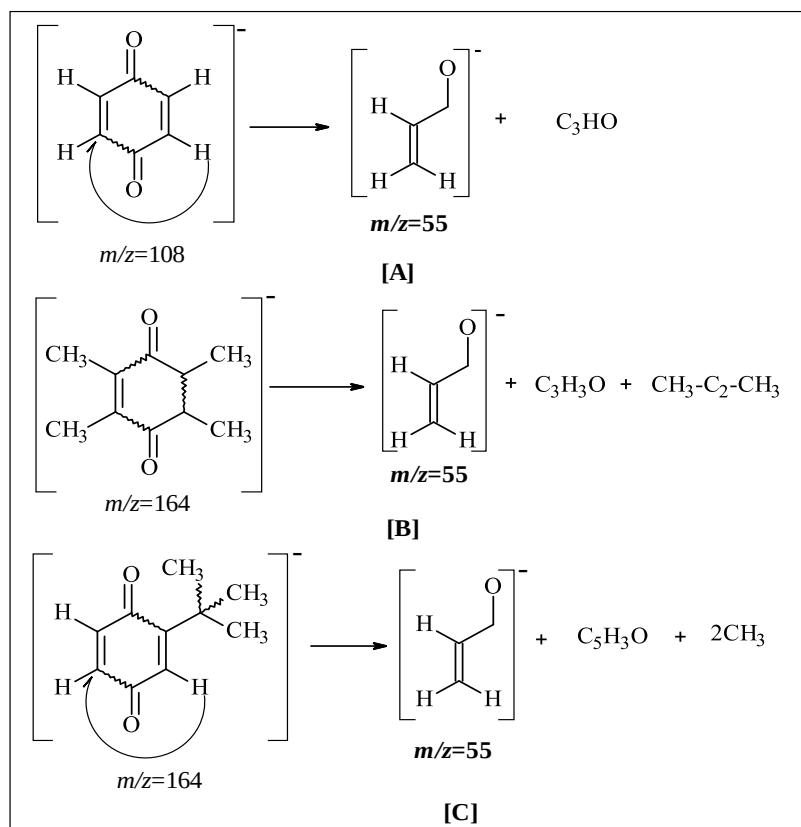


Scheme 4.5: Theoretically calculated fragmentation pathways for the formation of $[\text{C}_3\text{HO}]^-$



Scheme 4.6: Theoretically calculated fragmentation pathways for the formation of $[C_3H_2O]^-$

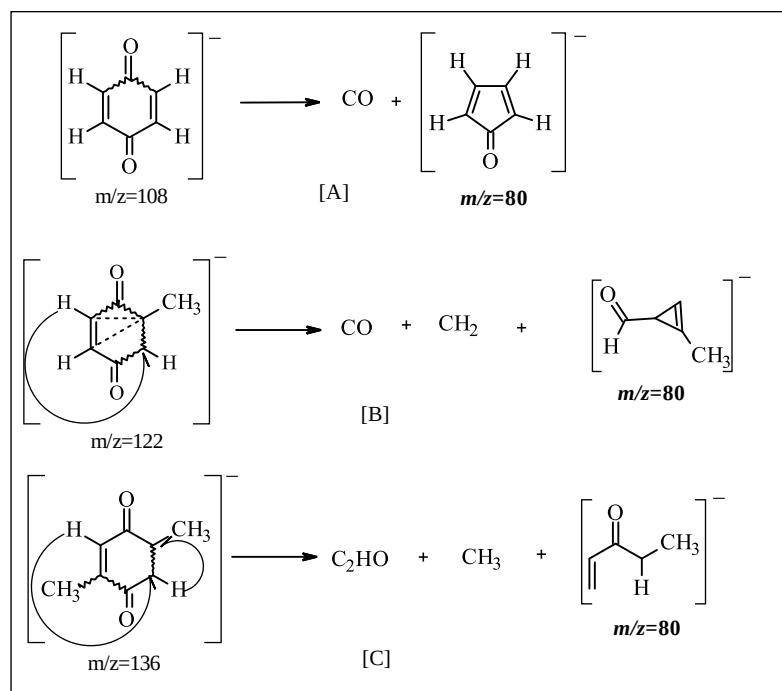
The fragmentation pathway of duroquinone to produce the fragment anion, $[C_3H_3O]^-$ with m/z 55 (**Scheme 4.7[B]**) is like the one illustrated in **Scheme 4.4[B]**-**[C]** for 2-methyl PBQ and 2,5-dimethyl PBQ. The same fragment anion is produced differently in PBQ and 2-tert-butyl PBQ. It is evident in **Scheme 4.7[A]** and **[C]** that H-atom migrates to a distant C-atom and the molecular anion breaks to form $[C_3H_3O]^-$ (m/z 55) and C_3HO in PBQ while in 2-tert-butyl PBQ C_5H_3O and two radicals of CH_3 in addition to C_3HO are formed.



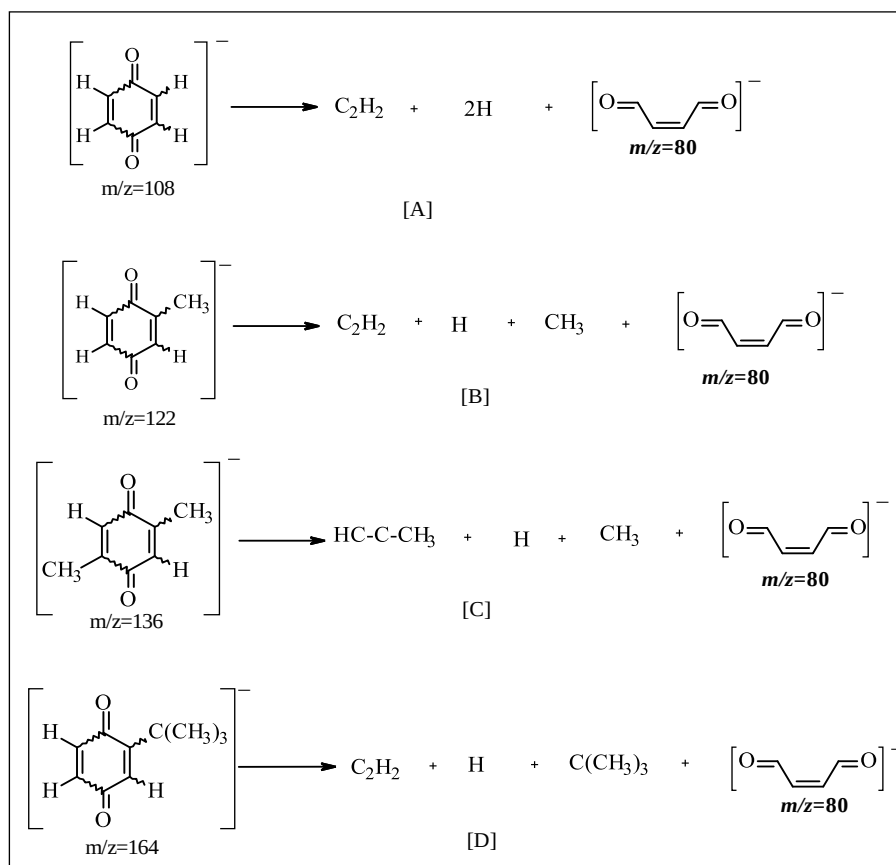
Scheme 4.7: Theoretically calculated fragmentation pathways for the formation of $[\text{C}_3\text{H}_3\text{O}]^{-}$

The fragment anion at m/z 80 had been significant in both the experimental and theoretical spectra of PBQ with the relative intensities of 6.4% and 12.8 % respectively. It was also discovered previously [6], and also in study with the aid of the calculations that the fragment m/z 80 could due to $[\text{C}_5\text{H}_4\text{O}]^{-}$ and $[\text{C}_4\text{O}_2]^{-}$ as illustrated in **Scheme 4.8** and **Scheme 4.9**. Elimination of the CO molecule from the molecular anion of PBQ produced a cyclopentadiene, $[\text{C}_5\text{H}_4\text{O}]^{-}$ with m/z 80, as shown in **Scheme 4.8[A]**. For 2-methyl PBQ and 2,5-dimethyl PBQ, elimination of CO/ C_2OH was speculated to be accompanied by loss of CH_2/CH_3 respectively, resulting in the formation of $[\text{C}_5\text{H}_4\text{O}]^{-}$, **Scheme 4.8[B]** and **[C]** shows. $[\text{C}_5\text{H}_4\text{O}]^{-}$, is unavailable in theoretical calculation of 2-tert-butyl PBQ. But when the molecular anion eliminated acetylene, C_2H_2 , and all the H-atoms in PBQ, anion, $[\text{C}_4\text{O}_2]^{-}$ was formed as shown in **Scheme 4.9 [A] (ii)**. Likewise, methyl PBQs undergo the same fragmentation but in addition to all the methyl group substituents were also eliminated to form $[\text{C}_4\text{O}_2]^{-}$ as seen in **Scheme 4.9 [B]-[D]**. Furthermore, the calculations showed $[\text{C}_5\text{H}_4\text{O}]^{-}$ is the most abundant fragment anion. $[\text{C}_5\text{H}_4\text{O}]^{-}$ contributed approximately 86.7% to the overall intensity of the fragment anion with

m/z 80 in PBQ. Similarly, in 2-methyl PBQ the contributions are 50% for $[C_5H_4O]^-$ and 50% $[C_4O_2]^-$. For 2,5-dimethyl PBQ these are 54% for $[C_5H_4O]^-$ and 46% $[C_4O_2]^-$. Comparatively, in 2-tert-butyl PBQ only $[C_4O_2]^-$ (and thus contributing 100% to the m/z 80) was produced at a very low intensity of 0.5%. Owing to these calculations, one may conclude that m/z 80 was mainly due to the anionic fragment $[C_5H_4O]^-$. Also, the availability of methyl groups to PBQ ring seems to disfavour the formation of $[C_5H_4O]^-$.

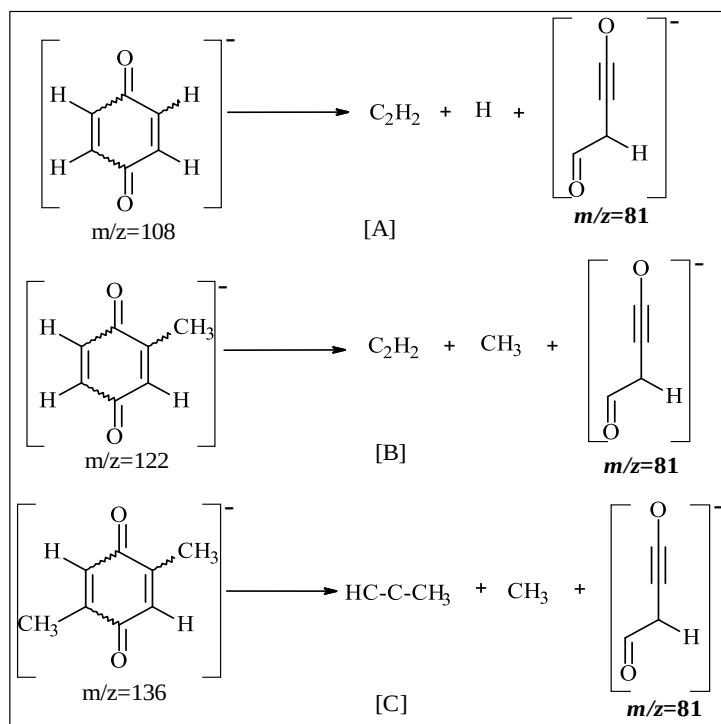


Scheme 4.8: Theoretically calculated fragmentation pathways for the formation of $[C_5H_4O]^-$



Scheme 4.9: Theoretically calculated fragmentation pathways for the formation of $[C_4O_2]^-$

Scheme 4.10 illustrates the theoretically calculated fragmentation pathway of the molecular anions of methylated PBQs to form the fragment anion with m/z 81. It is evident that the fragmentation is comparable to the one illustrated in **Scheme 4.9**, but here, one of the H-atoms remain attached to the ring. As shown in **Table 4.4** also, the relative intensity of the peak corresponding to this $[C_4HO_2]^-$ increases with increase in number of methyl groups attached to the PBQ ring. As a result, the presence of methyl groups on PBQ favours the formation of $[C_4HO_2]^-$ because the methyl groups introduced increase the electron density in the π -system of PBQ through positive inductive and resonance effect. This reduces uneven distribution of charges in PBQ hence increasing its ability to form $[C_4HO_2]^-$.



Scheme 4.10: Theoretically calculated fragmentation pathways for the formation of $[C_4HO_2]^-$

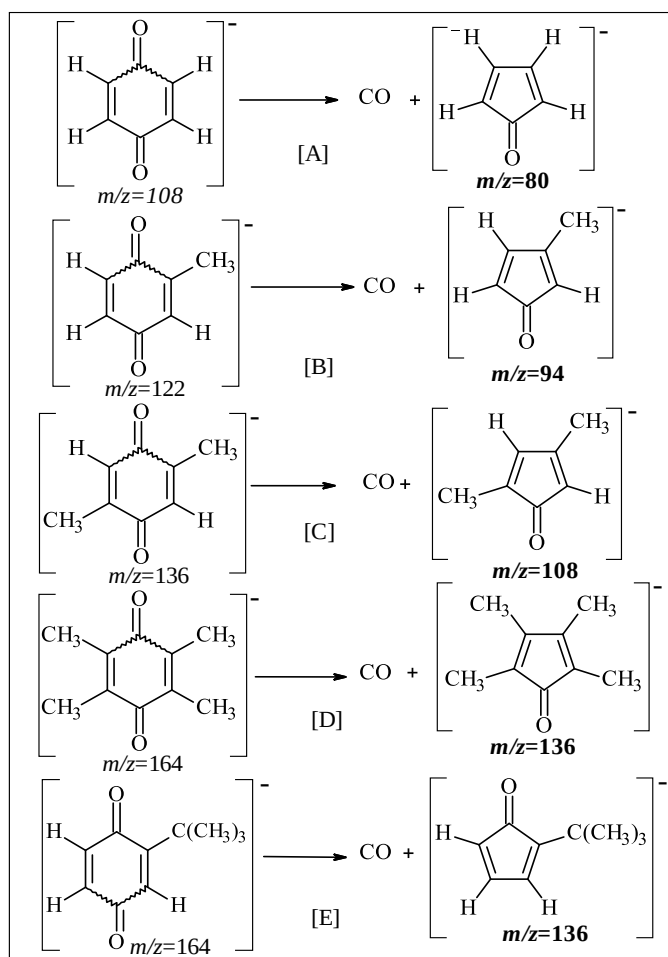
4.2.1.2 Formation of $[M-CO]^-$ fragment

Both theoretical and experimental mass spectra of methylated PBQs show the presence of $[M-CO]^-$. **Table 4.5** summarises observations made from NCIMS in **Figure 4.4-Figure 4.7**. As the number of methyl substituents to PBQ ring increased, the relative intensity of $[M-CO]^-$ decreased, as a result, methyl groups seemed to reduce the formation of $[M-CO]^-$. This was because the methyl groups released electron density towards the PBQ π -system through positive inductive and resonance effects. This reduced uneven distribution of charges in PBQ hence reducing its ability to eliminate CO. The positive inductive effect became more apparent when the methyl group was replaced by the tert-butyl substituent. The intensity dropped significantly due to the more electron donating ability of the tert-butyl substituent compared to the methyl groups. The steric hindrance offered by the tert-butyl substituent compared to methyl group when eliminating CO could also have contributed to a decrease in intensity. In duroquinone the repulsive force of π -electron cloud around the electrophilic carbon was increased by having four methyl groups on the ring, and this could have reduced the chances of eliminating

CO from the molecular anion [80]. The theoretically calculated fragmentation pathways for the formation of $[M-CO]^-$ are shown in **Scheme 4.11**.

Table 4.5: The $[M-CO]^-$ fragment of methylated PBQs with their corresponding relative intensities (*NB: (**Bold**) experimental relative intensities*).

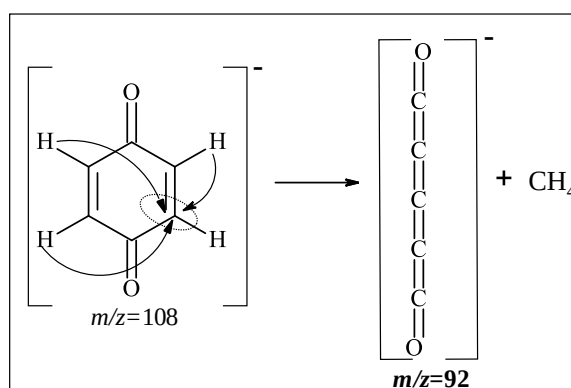
$[M-CO]^-$	PBQ	2-methyl PBQ	2,5-dimethyl PBQ	Duroquinone	2-tert-butyl PBQ
m/z	80	94	108	136	136
Relative Intensity (%)	12.8 (6.4)	6.2 (3.0)	6.4 (5.0)	1.1 (1.8)	0.8 (0.0)



Scheme 4.11: Theoretically calculated fragmentation pathway for the formation of $[M-CO]^-$

4.2.1.3 Origin of $[M-CH_4]^-$ and $[M-2H]^-$ in the experimental spectra

There is a significant peak observed in the experimental mass spectra of PBQ at m/z 92 which was absent in the theoretical spectra. The peak has previously been observed [6], at relatively low intensity of 0.06% corresponding to emission of either O or CH_4 or $[CH_2 + H_2]$. According to the Modified Neglect of Diatomic Overlap (MNDO) calculations done in that study, the minimal total energy for the formation of $[M-CH_4]^-$ was lower than that of $[M-O]^-$ and $[M-(CH_2 + H_2)]^-$. As illustrated in **Scheme 4.12**, the formation of $[M-CH_4]^-$ involves the migration of H-atoms to the same C-atom, the opening of the ring and the breaking down of the C=C bond. As a result, CH_4 was eliminated and two extra double bonds were formed to compensate for the distraction, forming a long chain with more extensive conjugated fragment, $[C_5O_2]^-$ with improved stability.

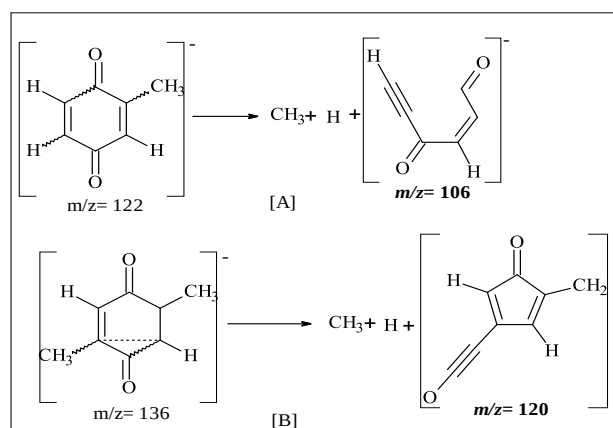


Scheme 4.12: Fragmentation pathway for the formation of $[M-CH_4]^-$ in PBQ. Adapted from [6].

The experimental mass spectra of methylated PBQs also showed the existence of $[M-CH_4]^-$, **Table 4.6** displays these anions with their corresponding m/z . The fragmental anions were absent or produced at relatively low intensities in theoretical mass spectra. According to this work's calculations, the formation of $[M-CH_4]^-$ in 2-methyl PBQ and 2,5-dimethyl PBQ, first involves elimination of CH_3 followed by elimination H-atom as illustrated in **Scheme 4.13**. Also, elimination of CH_4 from 2,5-dimethyl PBQ results in a hyper conjugated system with increased stability. In addition, it is also possible that this fragment anion could be due to fragmentation of anions with m/z greater than the molecular anions formed due to attachment of alkyl groups or impurities (O/ OH/ H_2O) to the molecule before ionisation [79], for example $[(M + C_3H_5) - (2CO + H)]^-$.

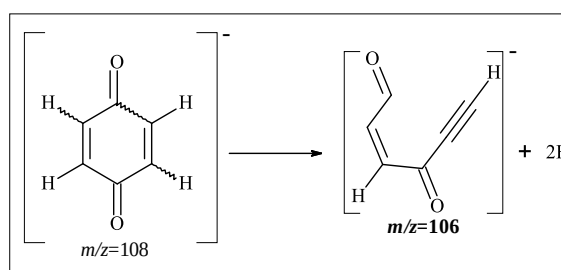
Table 4.6: The $[M-CH_4]^-$ of methylated PBQs corresponding to their m/z and relative intensities. (NB; (**Bold**) theoretical relative intensities).

$[M-CH_4]^-$	PBQ	2-methyl PBQ	2,5-dimethyl PBQ	Duroquinone	2-tert-butyl PBQ
m/z	92	106	120	148	148
Relative Intensity (%)	9.8 (0)	2.4 (0.26)	2.4 (1.14)	0.4 (0)	6.4 (0)



Scheme 4.13: Theoretically calculated fragmentation pathway for the formation of $[M-CH_4]^-$.

In addition, the experimental spectra also showed the existence of $[M-2H]^-$ anions for all the molecules. The peak was available in the theoretical spectrum of PBQ at m/z 106. **Scheme 4.14** illustrates the formation of this fragment anion.



Scheme 4.14: Theoretically calculated fragmentation pathway for the formation of $[M-2H]^-$ in PBQ

4.2.2 ECNCIMS of 2,6-dimethoxy PBQ

The experimental mass spectrum of 2,6-dimethoxy PBQ in **Figure 4.8** showed more fragment anions compared to the theoretical spectrum. Besides a 100% molecular anion peak at m/z 168, other peaks were observed in both spectra of 2,6-dimethoxy PBQ at m/z 95, 110, 123, 140 and 153. In addition, the theoretical spectrum also showed peaks at m/z 31, 41, 137 and 167. Like methyl PBQs, the experimental mass spectrum of 2,6-dimethoxy PBQ also displayed anions with m/z greater than that of the molecular anion, as presented in **Table 4.7**. Different from methyl PBQs the experimental spectrum showed more fragment anions (m/z 82, 94, 111, 112, 124, 126, 127, 138, 139, 142, 150, 151, 152, 154, 155 and 166) which were not observed in the theoretical spectrum. Plausible fragment anions presented in **Table 4.8** corresponding to these peaks were proposed in this work. The absence of these peaks in the theoretical spectra could have been due to the inadequacy of the theoretical method to describe the system.

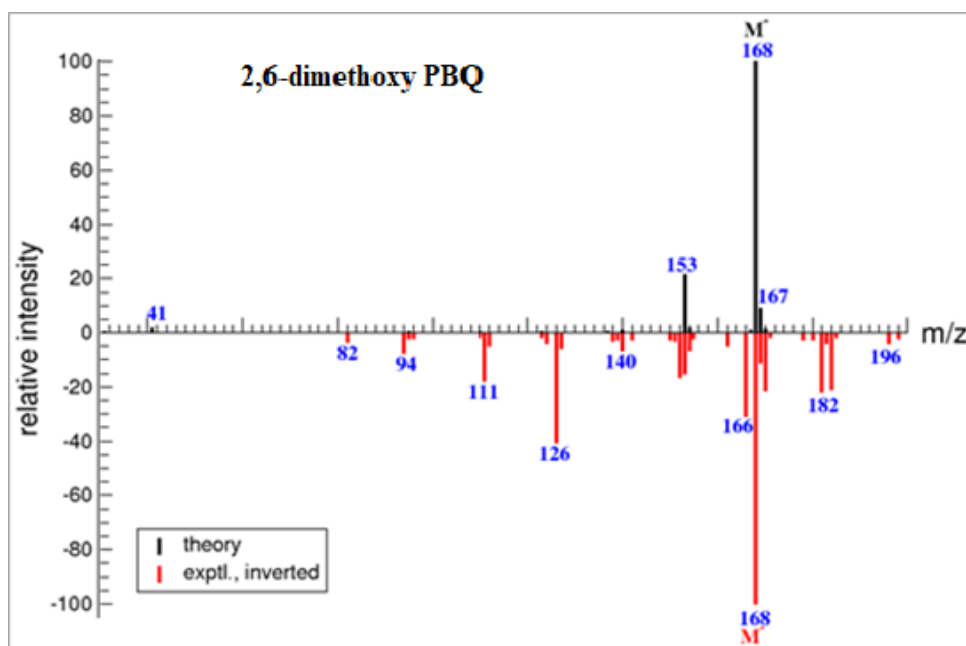


Figure 4.8: The theoretical and experimental mass spectra of 2,6-dimethoxy PBQ

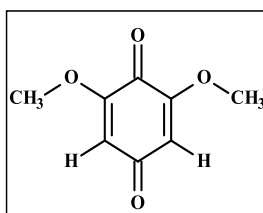


Figure 4.9: The structure of 2,6-dimethoxy PBQ

Table 4.7: Peaks of anions with higher m/z values than the molecular anion observed in the experimental spectrum of 2,6-dimethoxy PBQ. (**NB:** M is the structure of 2,6-dimethoxy PBQ represented in **Figure 4.9**.)

Anion Formed	m/z	Relative Intensity (%)
$[M+2H]^-$	170	21.5
$[M+3H]^-$	171	1.7
$[M+C-2H]^-$	178	2.5
$[M+C]^-$	180	2.7
$[M+CH_2]^-$	182	22.1
$[M+CH_3]^-$	183	3.8
$[M+O]^-$	184	21.0
$[M+OH/CH_5]^-$	185	1.6
$[M+C_2H_4]^-$	196	4.1
$[M+H+C_2H_5]^-$	198	2.5

Table 4.8: Peaks observed in the experimental spectra of 2,6-dimethoxy PBQ with their corresponding relative intensities and proposed fragment anions

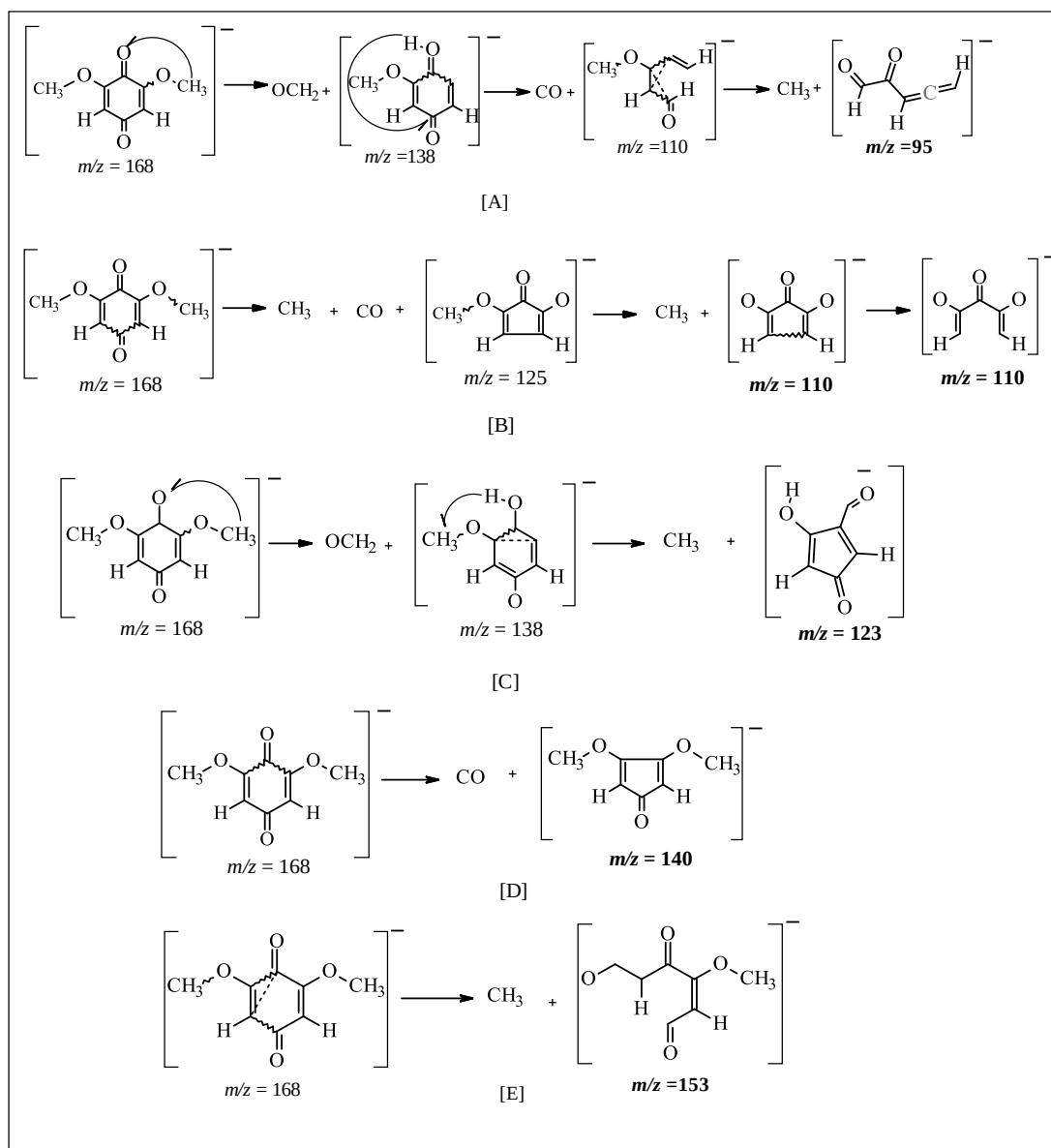
m/z	Relative intensities	Fragmentation of anion with greater m/z
82	3.7	$[M-(CH_3O+C_2)]^-$
94	7.5	$[M-(CH_3+OCH_3+CO)]^-$
111	17.7	$[M-(C_2H_2O+CH_3)]^-$
112	5.0	$[M-(C_2HO+CH_3)]^-$
124	3.8	$[M-(CH_3O+CH)]^-$
126	40.5	$[M-C_2H_2O]^-$
127	5.9	$[M-C_2HO]^-$
138	2.9	$[M-CH_2O]^- / [M-2CH_3]^-$
139	2.6	$[M-CHO]$
142	2.7	$[M-C_2H_2]^-$
150	2.5	$[M-H_2O]^-$
151	3.2	$[M-CH_5]^- / [M-OH]^-$
152	16.7	$[M-CH_4]^- / [M-O]^-$
154	6.8	$[M-CH_2]^-$
155	2.3	$[M-CH]^-$
166	30.6	$[M-2H]^-$

NB: M is the structure of 2,6-dimethoxy PBQ represented in **Figure 4.9**

4.2.2.1 Origin of peaks with m/z 95, 110, 123, 140 and 153 observed in the mass spectra

Both the experimental and theoretical mass spectra of 2,6-dimethoxy PBQ in **Figure 4.8** show peaks at m/z 95, 110, 123, 140 and 153. As seen, the peaks were produced at relatively higher intensities in the experimental spectrum while in theoretical spectrum they were produced at lower intensities except peak at m/z 153. The fragmentation pathways for the formation of the fragment anions

corresponding to these peaks were revealed through the calculation in this work, as illustrated in **Scheme 4.15**.



Scheme 4.15: Theoretically calculated fragmentation pathways of 2,6-dimethoxy PBQ molecular anion to form fragment anions with m/z 95, 110, 123, 140 and 153.

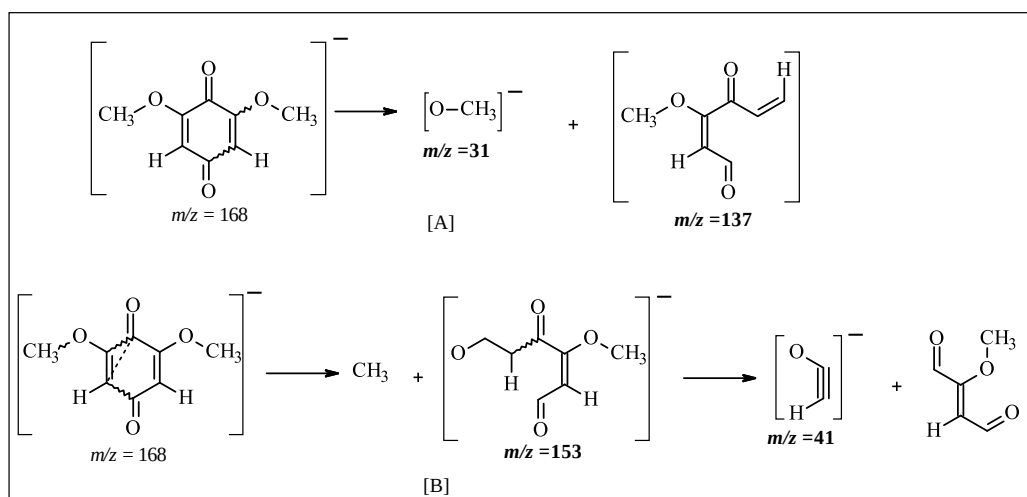
The peak at m/z 95 was speculated to correspond to $[C_5H_3O_2]^-$. Upon electron attachment, the molecular anion first eliminates CH_2O radical after migration of the H atom from methoxy group to the O atom in the CO adjacent to the methoxy groups. As seen in **Scheme 4.15 [A]**, the fragment anion with m/z 138 was formed which further dissociated by eliminating the CO adjacent to the methoxy groups

after an H atom had migrated from O atom (CO adjacent to methoxy groups) to the C atom (CO distal to methoxy groups). This dissociation resulted in the formation of $[\text{C}_6\text{H}_6\text{O}_2]^-$ with m/z 110. $[\text{C}_6\text{H}_6\text{O}_2]^-$ further eliminated CH_3 after several rearrangements to form the fragment anion, $[\text{C}_5\text{H}_3\text{O}_2]^-$ with m/z 95. For the formation of $[\text{C}_5\text{H}_2\text{O}_3]^-$ with m/z 110, the molecular anion eliminated the CO distal to the methoxy groups, followed by elimination of CH_3 and then $[\text{C}_6\text{H}_5\text{O}_3]^-$ was formed. $[\text{C}_6\text{H}_5\text{O}_3]^-$ further lost another CH_3 and as a result $[\text{C}_5\text{H}_2\text{O}_3]^-$ was formed, see Scheme 4.15 [B]. The molecular anion also eliminated CH_2O to form, $[\text{M}-\text{OCH}_2]^-$ with m/z 138. The mechanism in Scheme 4.15[C] shows migration of the H atom from the methoxy group (CH_3O) to CO group before emission of CH_2O . The fragment anion, $[\text{M}-\text{CH}_2\text{O}]^-$ further dissociated by eliminating CH_3 attached to the methoxy group. Elimination of CH_3 caused migration of H atom from the oxygen of the CO group to oxygen of the methoxy group (where the CH_3 detached). This fragmentation produced the fragment anion with m/z 123. Scheme 4.15[D] and Scheme 4.15[E] show the plausible fragmentation of the molecular anion to produce the $[\text{M}-\text{CO}]^-$ at m/z 140 and $[\text{M}-\text{CH}_3]^-$ at m/z 153 respectively.

4.2.2.2 Origin of peaks at m/z 31, 41, 137 and 167 observed in the theoretical mass spectra

It is evident in the theoretical spectrum of 2,6-dimethoxy PBQ Figure 4.8 that peaks at m/z 31, 41, 137 and 167 are absent from the experimental spectrum. Because the mass spectrometer was set to scan from 50, peaks at m/z 31 and 41 were not expected to be seen in the experimental mass spectrum while the peaks at m/z 137 and 167 were not observed due to the insensitivity of the mass spectrometer to detect them or maybe the theoretical method used may not have been accurate enough and a more advanced method could have given better results. According to the calculations of this work, the peak at m/z 31 (0.71 %) was speculated to correspond to $[\text{CH}_3\text{O}]^-$. Upon electron attachment, the molecular anion dissociates into $[\text{CH}_3\text{O}]^-$ and $\text{C}_7\text{H}_5\text{O}_3$ radical as illustrated in Scheme 4.16[A]. From the calculations, both CH_3O and $\text{C}_7\text{H}_5\text{O}_3$ were emitted as neutral or anionic fragments. This means that in some molecular dynamic's trajectories, based on the calculated charges and electron affinities, the two fragments could be assigned as $([\text{CH}_3\text{O}]^-$ and $\text{C}_7\text{H}_5\text{O}_3)$ or $([\text{C}_7\text{H}_5\text{O}_3]^-$ and $\text{CH}_3\text{O})$

When the molecular anion eliminated CH_3 , the $[\text{C}_7\text{H}_5\text{O}_4]^-$ at m/z 153 was formed. This fragment anion further dissociated into $\text{C}_5\text{H}_4\text{O}_3$ radical and $[\text{C}_2\text{HO}]^-$ with m/z 41, as illustrated in **Scheme 4.16[B]**.



Scheme 4.16: Theoretically calculated fragmentation pathways of 2,6-dimethoxy PBQ molecular anion to form fragment anions with m/z 31, 41, 137 and 167. NB; Mmechanism [A] has two types of species, in which the charges are switched.

4.2.3 NIMS of halogenated PBQs

Both the experimental and theoretical mass spectra of the halogenated compounds of PBQ in **Figure 4.10-Figure 4.13** showed less fragments and a few peaks with m/z greater than that of the molecular anion and halides form the base peak of the spectra. The Cl^- in both mono and dichloro PBQs showed isotopic peaks for Cl-35 and Cl-37 which agree with the expected natural abundances. The spectra of 2,5-dichloro PBQ and 2,6-dichloro PBQ in **Figure 4.11** and **Figure 4.12** respectively, showed one extra isotopic peak corresponding to the molecular anions with both Cl-35 and Cl-37 at m/z 178. The relative intensities of these peaks (i.e., 176, 178 and 180), decrease with increase in m/z .

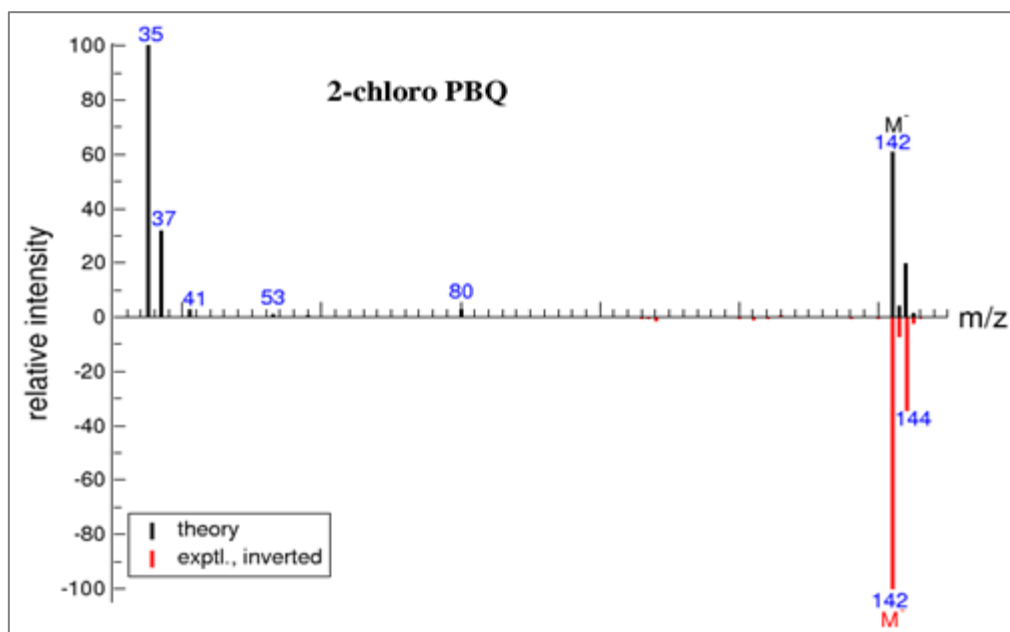


Figure 4.10: The theoretical and experimental mass spectra of 2-chloro PBQ

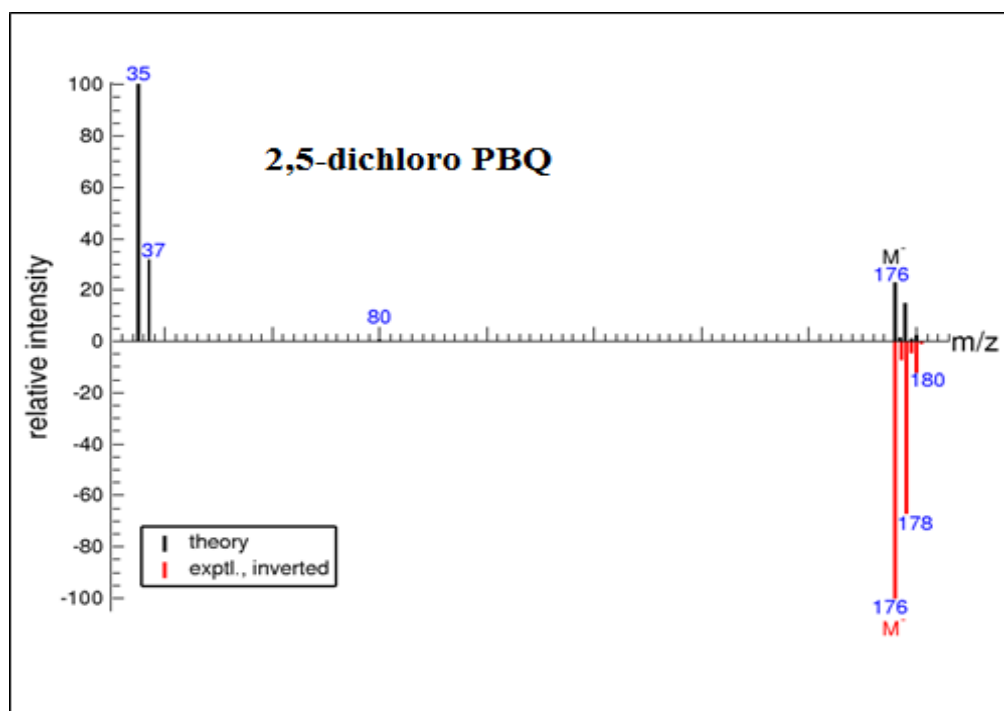


Figure 4.11: The theoretical and experimental mass spectra of 2,5-dichloro PBQ

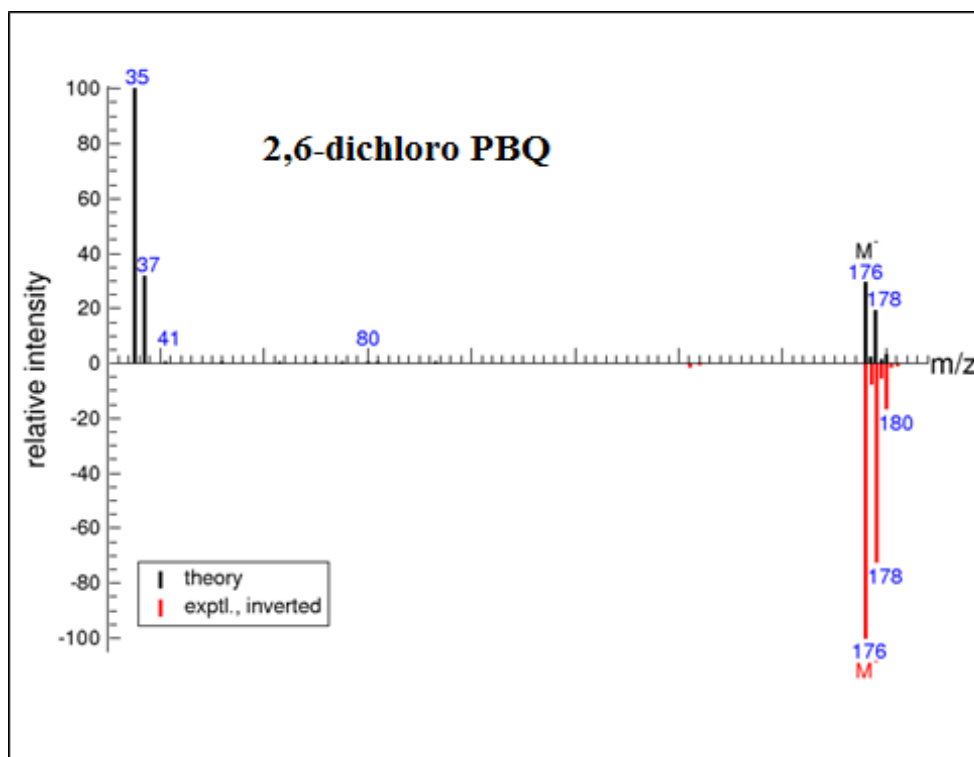


Figure 4.12: The theoretical and experimental mass spectra of 2,6-dichloro PBQ

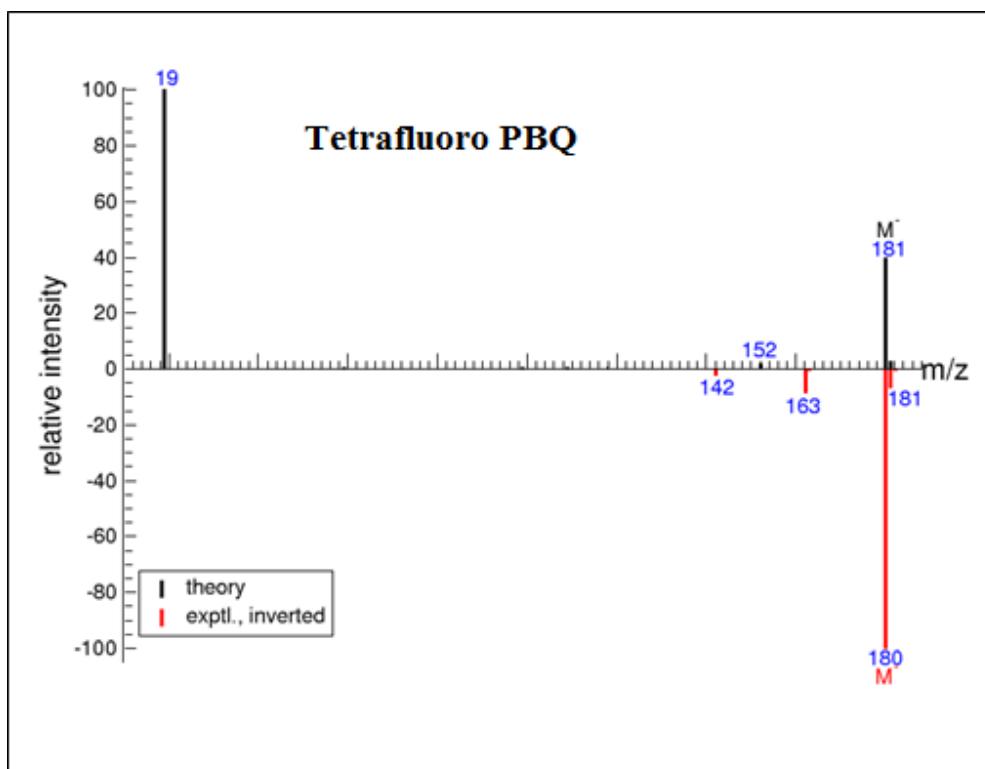


Figure 4.13: The theoretical and experimental mass spectra of tetrafluoro PBQ

Experimental spectra of halogenated PBQs are highly sensitive to even small changes to sample concentration, moderating gas pressure, temperature, and H₂O/O₂ contaminants [76]. Commonly appearing peaks in the experimental mass spectra of halogenated PBQs corresponds to the formation of M⁻ and [M-H]⁻, anions from various losses of X and HX, combination of, X⁻, X₂ and HX₂ (X=halogen). In addition, the presence of traces of O₂ and/or H₂O may result in [M+H-X]⁻, [M+O-X]⁻ and [M+OH-X]⁻. For this reason, the theoretical and experimental spectra of halogenated PBQs differ. **Table 4.9** shows anionic fragments observed in the experimental spectra. As previously explained, the mass spectrometer was set to scan from *m/z* 50, and therefore the fragments with *m/z* less than 50 in experimental spectra were not observed.

Table 4.9: Anionic fragments of halogenated PBQs observed in the experimental spectra.

Anion fragments	<i>m/z</i> (Relative intensities in %)			
	2-chloro PBQ	2,5-dichloro PBQ	2,6-dichloro PBQ	Tetrafluoro PBQ
[M-X] ⁻	107 (0.24)	-	-	-
[M-HX] ⁻	106 (0.53)	-	-	-
[M-2X] ⁻	-	-	-	142 (2.10)
[M+H-X] ⁻	108 (1.29)	-	142, 144 (1.44, 0.47)	162 (8.30)
[M+O-HX] ⁻	122 (0.74)	-	-	-
[M+OH-X] ⁻	124 (0.24)	-	-	-

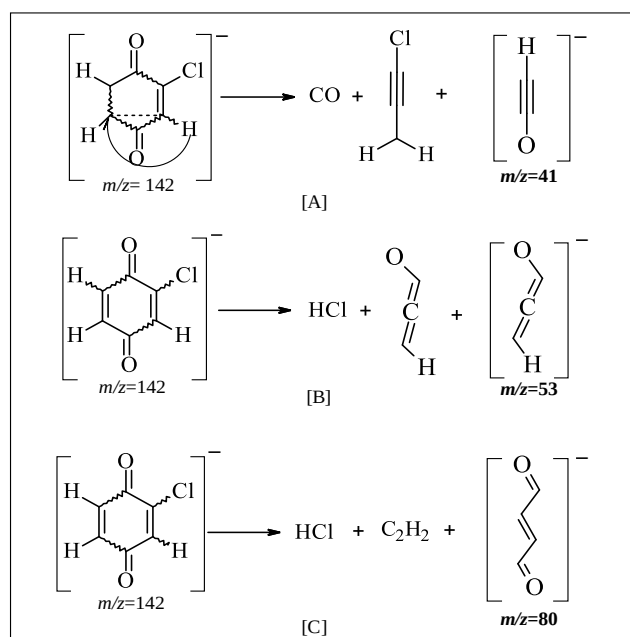
The theoretical mass spectra of chlorinated PBQs showed the presence of only three fragments, summarized in **Table 4.10**. The spectrum of 2-chloro PBQ had three strong peaks at *m/z* 41, 53 and 80, that of 2,5-dichloro PBQ had only one weak peak at *m/z* 80 and 2,6-dichloro PBQ had three peaks with relatively low intensities. On the other hand, the spectrum of tetrafluoro PBQ in **Figure 4.13** showed the molecular anion peak (*m/z* 180) and anion fragments with *m/z* 19 and 152.

Table 4.10: Anion fragments of chlorinated PBQs observed in theoretical spectra.

m/z	Relative intensity (%)		
	2-chloro PBQ	2,5-dichloro PBQ	2,6-dichloro PBQ
41	2.9	-	0.6
53	1.0	-	0.6
80	2.7	0.6	0.6

4.2.3.1 Fragmentation of 2-chloro PBQ

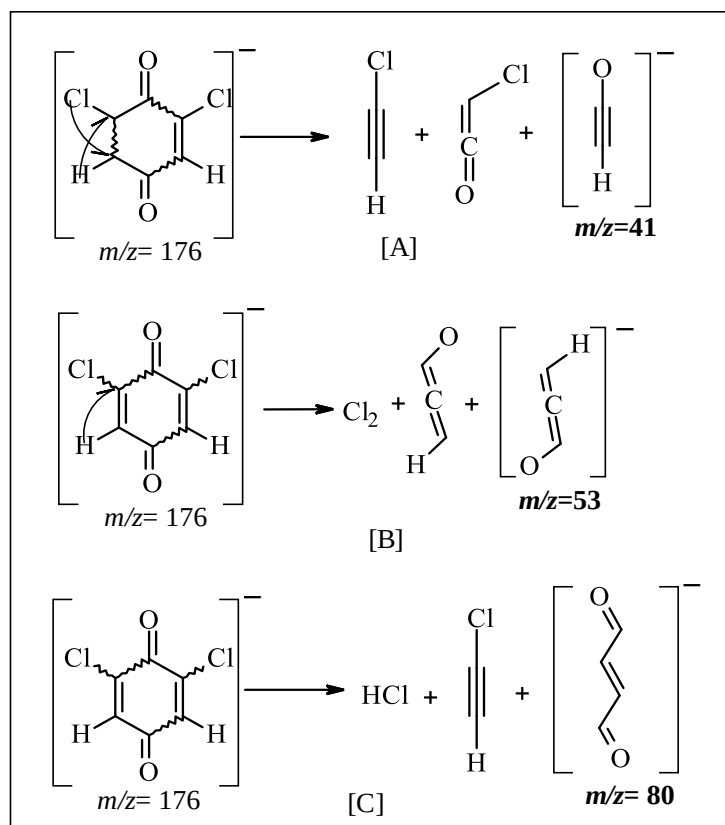
The fragmentation of 2-chloro PBQ shown in **Scheme 4.17** involved the opening of the ring, loss of Cl^- and migration of the H-atom. When forming $[\text{C}_2\text{HO}]^-$ with m/z 41, elimination of CO and migration of H-atom from C-3 to C-5 occurred after the ring opened, then the molecular anion split into $[\text{C}_2\text{HO}]^-$ and $\text{C}_3\text{H}_2\text{Cl}$ radicals, as seen in **Scheme 4.17[a]**. The other anion formed was $[\text{C}_3\text{HO}]^-$ with m/z 53. This anion was produced when the molecular anion lost the Cl and H atoms in C-6, then it split into halves after numerous structural rearrangements producing $[\text{C}_3\text{HO}]^-$ and C_3HO radicals as shown in **Scheme 4.17[b]**. Lastly, $[\text{C}_4\text{O}_2]^-$ with m/z 80 (**Scheme 4.17[c]**) was formed due to loss of the Cl and H atoms in C-2 and C_2H_2 respectively.



Scheme 4.17: Theoretically calculated fragmentation pathways of 2-chloro PBQ molecular anion.

4.2.3.2 Fragmentation of 2,5-dichloro PBQ and 2,6-dichloro PBQ

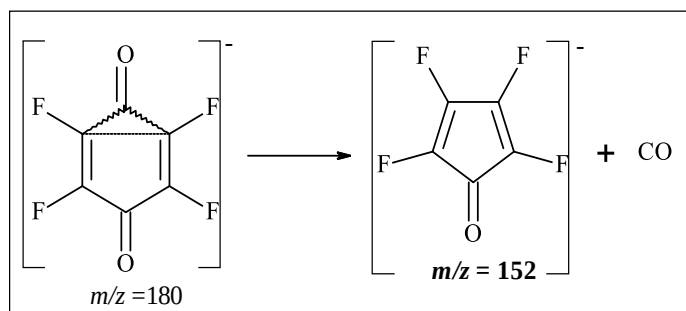
Table 4.9 shows fragment anions of 2,5-dichloro PBQ and 2,6-dichloro PBQ. The peak intensities for these fragments were very weak (all at 0.6%). Even though they were produced at relatively low intensities, the calculations showed the plausible fragmentation pathways to produce these fragments (**Scheme 4.18**). For the formation of $[\text{C}_2\text{HO}]^-$ (m/z 41) in 2,6-dichloro PBQ (**Scheme 4.18[a]**), loss of the Cl atom in C-6 initiated elimination of C_2HCl , migration of the H atom from C-5 to C-6 and the breakdown of C=C bond. As a result, $[\text{C}_2\text{HO}]^-$ (m/z 41) and $[\text{C}_2\text{O}]^-$ were produced. $[\text{C}_2\text{O}]^-$ then attached to the Cl atom previously eliminated from C-6 to form C_2OCl . Not only $[\text{C}_2\text{HO}]^-$ was formed, but also $[\text{C}_3\text{HO}]^-$ with m/z 53 was formed during fragmentation of 2,6-dichloro PBQ. The pathway is illustrated in **Scheme 4.18[b]**. Loss of the Cl atom in C-2 lead to ring opening and migration of the H atom from C-5 to C-4, then that of C-4 to C-6. This caused elimination of another Cl atom in C-6 then the remaining fragment split into halves forming $[\text{C}_2\text{HO}]^-$ and C_2HO . The spectra of 2,6-dichloro PBQ also showed the existence of $[\text{C}_4\text{O}_2]^-$ with m/z 80. This fragment anion is produced when the molecular anion ring opens after eliminating the C atom in C-6. The Cl atom in C-2 also detaches, and the remaining fragment rearranges into a three membered ring. The previously detached Cl atom from C-2 re-attaches at C-6 after elimination of the H atom and C_2HCl radical. The H atom then bonds to Cl atom which detached previously from C-6 forming HCl , as illustrated in **Scheme 4.18[c]**. Similarly, 2,5-dichloro produced $[\text{C}_4\text{O}_2]^-$ but differently. Here the fragmentation involved the detachment of the Cl atom in C-2 followed by the ring opening and then detachment of the H atom. The remaining fragment then breaks into the C_2HCl radical and $[\text{C}_4\text{O}_2]^-$.



Scheme 4.18: Theoretically calculated fragmentation pathways of 2,6-dichloro PBQ molecular anion

4.2.3.3 Fragmentation of tetrafluoro PBQ

In addition to F^- (m/z 19), the theoretical spectrum of tetrafluoro PBQ also showed the formation of the fragment anion with m/z 152 which corresponded to $[\text{M}-\text{CO}]^-$, **Scheme 4.19**. However, it has been observed previously, [55], that in addition to F^- , there are several fragments produced upon attachment of a low energy electron to the neutral molecule. These fragments form when the molecular anion eliminates either one or two CO groups followed by loss of F-atom/s. The loss of one CO group is mostly associated with rearrangement to a five membered ring, as observed in this study, as illustrated in **Scheme 4.19** it has been reported that, fragments associated with additional loss of F-atom/s result in an open chain arrangement of $[\text{M} - \text{CO} - n\text{F}]^-$; $n = 1, 2, 3$ and 4 while the loss of two CO groups involves extensive fluorine migration and recombination of the anionic fragment to form a four-carbon chain, $[\text{F}_2\text{C}=\text{C}=\text{C}=\text{CF}_2]^-$ [55].



Scheme 4.19: Theoretically calculated fragmentation pathway of tetrafluoro PBQ molecular anion

4.2.4 General Summary on NCIMS

Generally, the ECNCIMS of PBQs produced less fragment ions as compared to the EI-MS and the most intense peaks corresponded to the formation of a well stabilized, long-lived molecular anion, M^- , where in the case of electron donating derivatives, they formed base peaks for the spectra. Since PBQs have large positive electron affinities, it was expected for these molecules to form stable molecular anions upon capturing an additional electron [75]. This stability increases when PBQ is substituted with electronegative substituents and reduces with electropositive substituents. For this reason, electron donating substituents increased the fragmentation of PBQ while electron withdrawing substituents reduced it. This was justified by many peaks observed in the spectra of PBQs with electron donating groups which were speculated to correspond to the fragment anions. The most commonly occurred fragment anions were mostly resulting from elimination of ethylene (or most substituted ethylene) and/ or carbonyl group, migration of the H atom to either nearby or distal C atom. Sometimes elimination of a substituent and rearrangement of the resultant fragment also occurred. In addition, there was elimination of HX, X and migration of X ($X = \text{Cl}, \text{F}$) observed in PBQs with electron withdrawing groups. Another observed fragment anion was Cl^- / F^- which formed the base peak of the spectra of PBQs with electron withdrawing groups.

4.3 Substituent Effect on Molecular Properties of PBQ

4.3.1 Substituent effect on the reduction potentials of PBQ

Reduction potentials (E_1 and E_2) are valuable when studying the stabilities of anions in solution. E_1 and E_2 of PBQs' under study were determined by cyclic voltammetry in an acetonitrile solution containing tetraethyl ammonium tetrafluoroborate, as the supporting electrolyte, referenced to an Ag/AgCl_(sat) redox couple. Representative cyclic voltammograms of 2-methyl PBQ, PBQ and 2-chloro PBQ are shown in **Figure 4.14**.

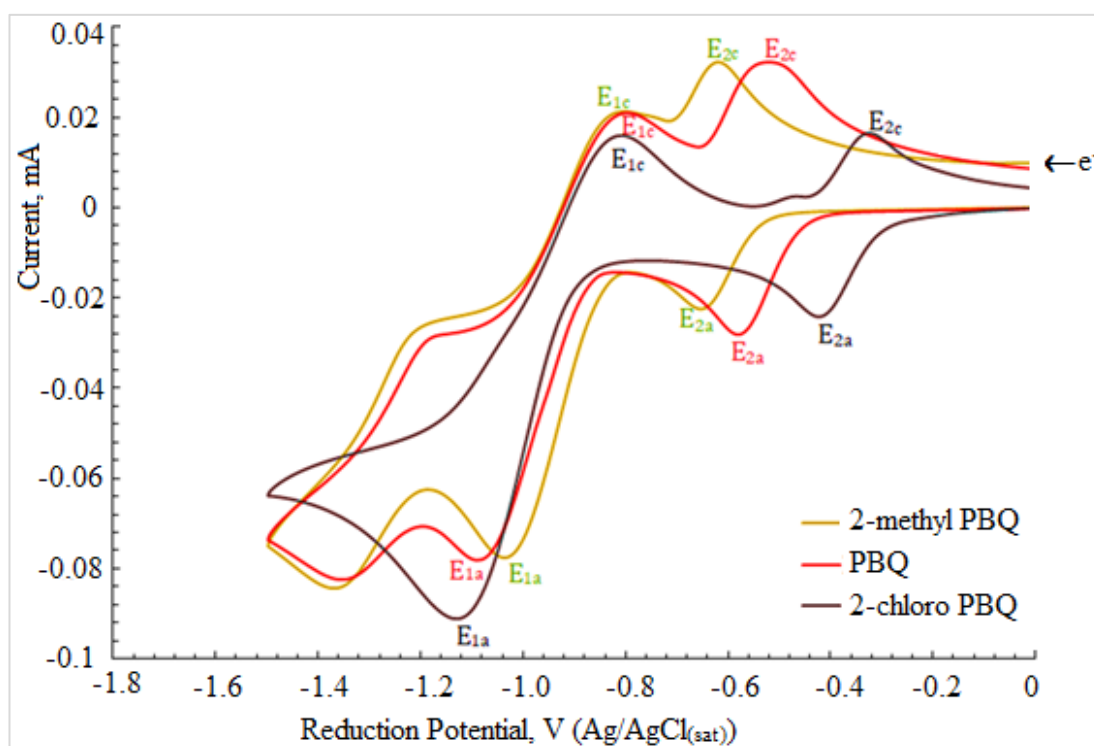


Figure 4.14: Representative cyclic voltammograms for 2-methyl PBQ, PBQ and 2-chloro PBQ in acetonitrile at 100 mV/s scan rate with a glassy carbon working electrode.

The E values were determined using **Equation 4.1**, where E_a and E_c represent the anodic and cathodic peak potentials, respectively.

$$E_1 = \frac{E_{1a} + E_{1c}}{2} \quad \text{and} \quad E_2 = \frac{E_{2a} + E_{2c}}{2} \quad \text{Equation 4.1}$$

As seen in **Figure 4.14** two sets of reversible redox peaks, which correspond to PBQ/PBQ^{•-} (E₁) and PBQ^{•-}/PBQ²⁻ (E₂) couples are revealed. But for this study only E₁ values will be used in the analysis because it proved to be more reversible and reproducible for all the compounds under study than E₂ values. Also, the tendency of the supporting electrolyte to form ion-pairs with the dianion in E₂ step limits the accuracy of the measured E₂ values [61].

Table 4.11 presents parameters from voltammetric curves. 2,6-dimethoxy PBQ has the most negative value of E₁ while tetrafluoro PBQ has the least negative value of E₁. The reduction potentials were strongly dependent on the nature of the substituents and the stability of the anion formed. The presence of electron donating substituents in PBQ decreases the ability of PBQ to form the molecular anion radical, shifting the E₁ to more negative value. On the other hand, the presence of electron withdrawing substituents in PBQ favours the reduction of PBQ to its molecular anion radical. The highest E₁ value in tetrafluoro PBQ was due to the strong interaction between the fluorine atoms and the quinone system via resonance effect whereas for 2,6-dimethoxy PBQ, the size and asymmetry of the substituent induce steric effects which shifts the E₁ to more negative value [81], [82].

Systematic trends were also observed within subsets of related PBQs'. E₁ values of PBQs decreased linearly with each introduction of methyl group due to inductive effect, with each additional methyl group shifting the E₁ to more negative value by 0.08 volts. Similarly, the correlation between E₁ values and the number of Cl atoms added was also observed. With each addition of Cl atom to PBQ system increasing E₁ values due to their strong electron withdrawing inductive effect which helped in stabilizing the negative charge of the reduced species, resulting in less negative values of E₁. There was also a slight difference between the E₁ values of 2,5- and 2,6-isomers of chlorinated PBQs indicating that the position of Cl atoms play an insignificant role in determining their stabilization [37], [83].

Table 4.11: Parameters from Voltammetric curves of PBQs.

Compounds	E _{1c}	E _{1a}	E _{2c}	E _{2a}	E ₁	E ₂	ΔE ₁	ΔE ₂	Literature value, E ₁
PBQ	-0.559	-0.561	-1.06	-0.835	-0.560	-0.948	0.002	-0.225	-0.52 ⁽ⁱ⁾
2-Methyl PBQ	-0.646	-0.625	-1.02	-0.833	-0.636	-0.927	-0.021	-0.187	-0.61 ⁽ⁱ⁾
2,5-Dimethyl PBQ	-0.727	-0.701	-1.05	-0.819	-0.714	-0.935	-0.026	-0.231	-0.68 ⁽ⁱ⁾
Duroquinone	-0.971	-0.783	-1.30	-1.20	-0.877	-1.250	-0.188	-0.100	-0.84 ⁽ⁱⁱ⁾
2-Tert-Butyl PBQ	-0.689	-0.647	-1.05	-0.825	-0.668	-0.938	-0.042	-0.225	
2,6-Dimethoxy PBQ	-1.06	-0.817	-	-	-0.939	-	-0.243	-	-1.05 ⁽ⁱⁱⁱ⁾
2-Chloro PBQ	-0.407	-0.348	-1.11	-0.839	-0.378	-0.975	-0.059	-0.271	-0.34 ⁽ⁱⁱ⁾
2,5-Dichloro PBQ	-0.268	-0.160	-1.07	-0.837	-0.214	-0.954	-0.108	-0.233	-0.18 ⁽ⁱ⁾
2,6- Dichloro PBQ	-0.235	-0.107	-0.843	-1.05	-0.171	-0.947	-0.128	0.207	-0.18 ⁽ⁱⁱ⁾
Tetrafluoro PBQ	-0.0617	-	-1.07	-	-0.031	-0.535	-0.062	-1.070	-0.03 ^(iv)

NB: All values of E were measured in volts, V. E_1 and E_2 represent peak potentials when $Q \rightarrow SQ^{\cdot-}$ (first reduction) and $SQ^{\cdot-} \rightarrow Q^{2-}$ (seconds reduction) respectively where Q is the quinone, $SQ^{\cdot-}$ is the semiquinone radical and Q^{2-} is the quinone dianion. Subscript (a) and (c) represent anode and cathode. $\Delta E = E_c - E_a$. All values are measured in volts. Literature values of E_1 obtained from (i) [83], (ii) [84], (iii) [81] and (iv) [47].

4.3.2 Substituent effect on the electron affinity of PBQ

As one of the fundamental quantities used to assess the ability of a molecule to accept an electron, the electron affinities (EAs) of PBQs were calculated according to the difference of the total energies of a molecule (PBQ) and the corresponding anion (PBQ⁻), when both species are in their ground vibrational and rotational states, as shown by **Equation 4.2** [50], [75]. A positive value of EA showed that anion was stable with respect to its neutral molecule.

$$EA = E_{PBQ} - E_{PBQ^-} \quad \text{Equation 4.2}$$

Both adiabatic (EA_a) and vertical (EA_v) electron affinities for PBQs under study were calculated and are presented in **Table 4.12**. EA_a is the energy difference between the neutral species and the anionic species at their respective optimized geometries (see **Equation 3.10**) while EA_v is the energy difference between the optimized geometry of the neutral and the anion state at the corresponding geometry of the neutral species (see **Equation 3.11**) [49], [64]. The difference between the

EA_a and EA_v indicates a significant nuclear relaxation from the neutral to anionic state of PBQs upon capturing an electron [49].

Table 4.12: Electron Affinities of PBQs calculated using DFT/B3LYP/ 6-311++G (d,p) and their corresponding values from literature.

Compound	Theoretical Vertical EA (eV)	Theoretical Adiabatic EA (eV)	Experimental EA (eV)
Tetrafluoro PBQ	2.68	3.04	2.70 ± 0.2 [54], [75], [85], [86] 2.92 ± 0.2 [15], [85]
2,5-dichloro PBQ	2.43	2.73	2.44 ± 0.2 [54], [75] 2.43 ± 0.2 [85]
2,6-dichloro PBQ	2.43	2.73	2.48 ± 0.2 [54], [75], [85], [86]
2-chloro PBQ	2.18	2.46	2.05 ± 0.15 [54]
PBQ	1.89	2.17	1.91 ± 0.2 [54], [75], [85], [86] 1.89 ± 0.2 [17], [85]
2-tert-butyl PBQ	1.83	2.11	1.84 ± 0.2 [85]
2-methyl PBQ	1.79	2.07	1.85 ± 0.2 [75], [85], [86] 1.79 ± 0.2 [54]
2,5-dimethyl PBQ	1.76	1.96	1.76 ± 0.2 [54], [75] 1.77 ± 0.2 [85]
2,6-dimethoxy PBQ	1.71	1.78	1.72 ± 0.1 [75] 1.73 ± 0.2 [85]
Duroquinone	1.52	1.80	1.62 ± 0.2 [54], [75] 1.59 ± 0.2 [85]

Both adiabatic electron affinity (EA_a) and vertical electron affinity (EA_v) were calculated. The calculated EA_v correlated well with available experimental values in the literature. The comprehensive comparison between the theoretically calculated EA_v and experimentally reviewed EA values verifies the reliability of the theoretical method (DFT/B3LYP/6-311++G(d,p)) employed. As seen in **Table 4.12**, the EA values calculated were positive and this signified that the anions are stable with respect to electron attachment [49], [87].

Introducing electron donating groups like alkyl and alkoxy into a PBQ structure decreased the EA while electron withdrawing groups (halogens) showed the

opposite effect. Notice the systematic trends within subgroups of related PBQs, including alkyl/alkoxy and halogenated PBQs. The EA values of PBQs decreased linearly per each introduction of a methyl substituent. The mono-, di-, tri- and tetramethyl substituted PBQs are separated by about 0.07 eV [87]. The destabilizing effect of methyl groups was due to their weak π and δ donor ability. 2,6-dimethoxy PBQ was slightly less destabilizing than duroquinone, and 2-tert-butyl substitution was the least destabilizing. The effect of halogen substitution on EA of PBQ is also shown. An increase with each chlorine substituent was quite large. This effect was previously observed in mono-, di-, trifluoro PBQs. There was a strong linear correlation ($R^2 = 0.998$) between EA and the number of fluorine atoms, each additional fluorine atom increased the EA by 0.2 eV [47]. The calculations also confirmed identical values of EA between 2,5- and 2,6-chloro PBQs as seen in experiments where they differed by 0.01 eV. It has also been reported from literature that similarly, for the disubstituted derivative of difluoro PBQ, the calculated EAs for those species were within 0.03 eV of one another [47]. This shows that the position of halogen atoms in PBQ do not play significant role in determining their stabilization effect. Additionally, **Table 4.12** reveals that four fluorine atoms increased substantially the EA by 0.79eV. In comparison to tetrachloro PBQ (EA = 2.78 eV), the four chlorine substituents increase the EA by 0.84eV, as a result chlorine substitution increases EA more than fluorine substitution [49], [75]. Since the Cl atom has large, diffuse electron clouds than the C atom (where Cl is bonded), it easily attracts electrons towards itself, an effect that has been shown to stabilize anions [48].

4.3.3 Relationship between reduction potential and electron affinity of PBQs.

The relationship between theoretical electron affinities and the experimental reduction potentials (E1) was also examined. **Figure 4.15** illustrates the resulting correlation. Linear correlation (with a correlation coefficient of 0.9885) was observed between two parameters. Since the slope in the plot of the E1 against EA is positive, one can conclude that EA consistently increased with increase in E1. As a result, PBQs with high electron affinities were easily reduced. PBQ derivatives with electron withdrawing substituents were easily reduced compared to those with electron donating groups [82], [84].

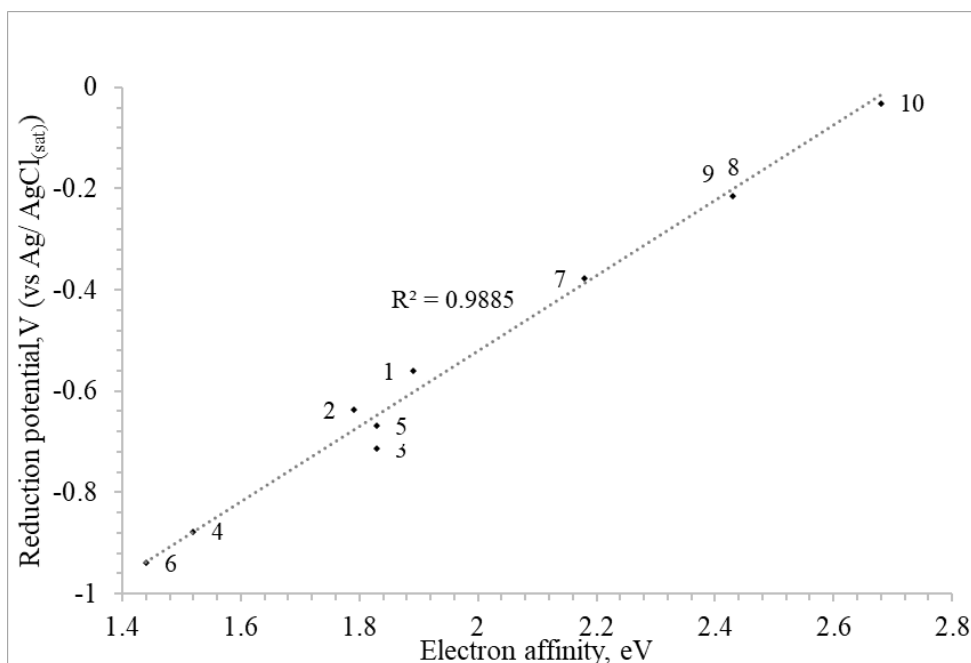


Figure 4.15: The correlation plot for experimentally determined reduction potentials (E_1) vs. calculated electron affinities of (1) PBQ; (2) 2-methyl PBQ; (3) 2,5-dimethyl PBQ; (4) duroquinone; (5) 2-tert-buty PBQ; (6) 2,6-dimethoxy PBQ; (7) 2-chloro PBQ; (8) 2,5-dichloro PBQ; (9) 2,6-dichloro PBQ; and (10) Tetrafluoro PBQ.

4.3.4 The influence of electron affinity on the response of the molecular anion

The electron affinity seemed to influence the signal intensity of producing the molecular anion during ECNCl. In **Figure 4.16** halogenated PBQs (7-10) produced their molecular anions at extremely higher intensities (<10 000 ion counts) while methyl and methoxy PBQs (2-6), showed low intensities (>10 000 ion counts). Halogens helped to disperse the negative charge of the reduced species and this increased stability of the molecular anion of PBQ. As a result, their mass spectra showed strong peaks of M^- . Electron donating substituents have a destabilizing effect on the molecular anion of PBQ. They tend to release electrons towards the PBQs ring conjugated system, and this increased the electron density within the ring which in turn decreases the stability of the anion formed. Unlike other methylated PBQs, duroquinone produced a very stable M^- irrespective of its low EA. This anomalous behaviour has been previously discovered [88]. Duroquinone was found to form a very stable, long-lived ($\tau=200\mu\text{s}$) molecular anion at electron impact energies of 1.8 eV. This explains the reason why the NCIMS of duroquinone have fewer fragments in **Figure 4.6**.

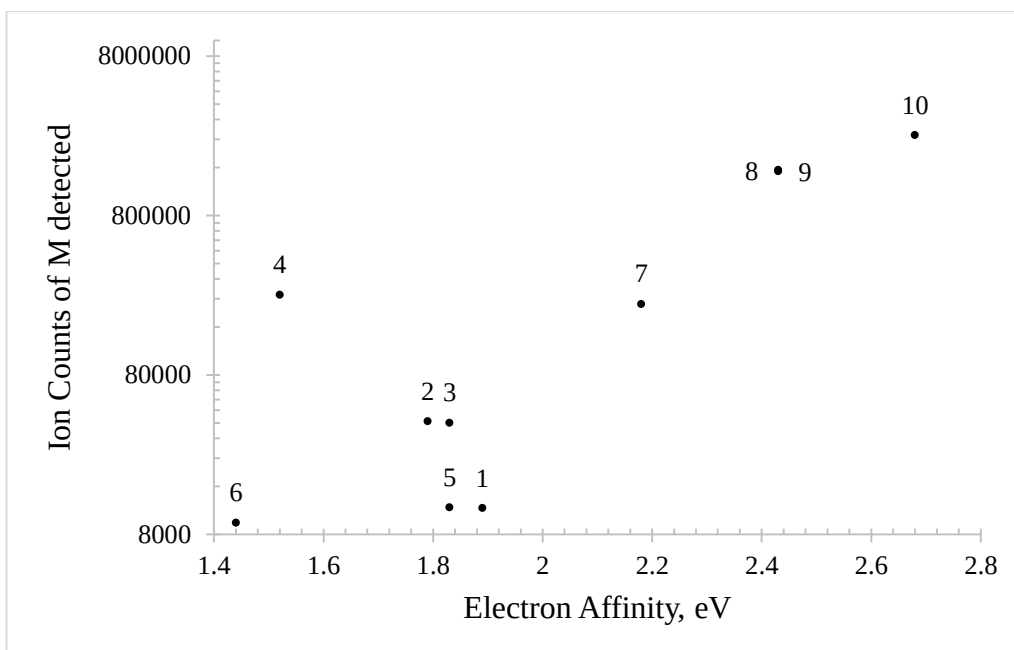


Figure 4.16: The influence of electron affinity on the response of M^- in ECNI of (1) PBQ; (2) 2-methyl PBQ; (3) 2,5-dimethyl PBQ; (4) duroquinone; (5) 2-tert-buty PBQ; (6) 2,6-dimethoxy PBQ; (7) 2-chloro PBQ; (8) 2,5-dichloro PBQ; (9) 2,6-dichloro PBQ; and (10) Tetrafluoro PBQ.

4.3.5 Substituent effect on the Geometrical parameters of PBQs

DFT calculations on the geometrical parameters of the neutral and anionic species of PBQ and its derivatives under study were calculated. **Table 4.13** presents the optimized geometrical parameters of the neutral and anionic species of PBQ and its electron donating derivatives. As seen, the calculated bond lengths of PBQ were in excellent agreement with bond lengths determined by electron diffraction [78]. The calculated C=O bond lengths in this work were 0.005 Å shorter than the ones determined by electron diffraction (1.225 Å) and that of C=C were slightly shorter, by 0.004 Å (electron diffraction C=C bond length is 1.344 Å). In contrast, the calculated C-C single bonds were only 0.005 Å longer than the experimentally determined bonds which were 1.481 Å. The bond angles calculated also agreed well with experiment and differed by an average of 0.3° and 0.8° for the C-C=C (121.0) and C-C-C (118.1) angles, respectively. This proved that 6-311G++(d,p) was a good method that could be used to predict optimized structural parameters.

Table 4.13: Geometrical parameters of PBQ and its electron donating derivatives with their anions calculated using B3LYP /6-311G++(d,p)

Structural parameter (bond length, Å and bond angle, °)																		
	neutral	anion	Δ	neutral	anion	Δ	neutral	anion	Δ	neutral	anion	Δ	neutral	anion	Δ			
C₁=O₁₂	1.220	1.266	0.046	1.221	1.267	0.046	1.221	1.267	0.046	1.223	1.271	0.048	1.222	1.269	0.047	1.226	1.265	0.039
C₄=O₁₁	1.220	1.266	0.046	1.220	1.266	0.046	1.221	1.267	0.046	1.223	1.269	0.046	1.221	1.266	0.045	1.207	1.258	0.051
C₂=C₃	1.340	1.371	0.031	1.346	1.373	0.027	1.344	1.373	0.029	1.350	1.378	0.028	1.349	1.376	0.027	1.350	1.374	0.024
C₅=C₆	1.340	1.371	0.031	1.338	1.370	0.032	1.344	1.373	0.029	1.350	1.378	0.028	1.337	1.368	0.031	1.350	1.374	0.024
C₁-C₂	1.486	1.450	-0.036	1.500	1.460	-0.040	1.500	1.458	-0.042	1.498	1.460	-0.038	1.508	1.469	-0.039	1.508	1.460	-0.048
C₁-C₆	1.486	1.450	-0.036	1.485	1.447	-0.038	1.478	1.446	-0.032	1.498	1.460	-0.038	1.488	1.447	-0.041	1.508	1.460	-0.048
C₄-C₅	1.486	1.450	-0.036	1.485	1.448	-0.037	1.500	1.458	-0.042	1.492	1.454	-0.038	1.480	1.444	-0.036	1.472	1.446	-0.026
C₃-C₄	1.486	1.450	-0.036	1.479	1.450	-0.029	1.478	1.446	-0.032	1.492	1.454	-0.038	1.480	1.450	-0.030	1.472	1.446	-0.026
C₆-C₁-C₂	117.3	114.8	-2.5	118.2	115.8	-2.4	118.4	115.9	-2.5	120.2	117.7	-2.5	118.6	116.2	-2.4	116.4	113.9	-2.5
C₃-C₄-C₅	117.3	114.8	-2.5	117.5	115	-2.5	118.4	115.9	-2.5	120.2	117.8	-2.4	117.7	116.3	-2.4	118.7	116.0	-2.7
C₁-C₂=C₃	121.3	122.6	1.3	119.1	120.7	1.6	118.6	120.2	1.6	119.7	121.0	1.3	117.7	119.0	1.3	121.2	123.2	2.0
C₄-C₅=C₆	121.3	122.6	1.3	120.8	122	1.2	118.6	120.2	1.6	120.1	121.3	1.2	120.0	121.3	1.3	121.3	121.9	0.6

Electron donating substituents increases the C=O and C=C bond lengths slightly while. The position of a substituent also played a vital role in determining the bond lengths. For example, the C=O bond adjacent to the substituents in 2-methyl, 2-tert-butyl, and 2,6-dimethoxy PBQs became longer than the distal C=O bond while in 2,5-dimethyl PBQ they were equal. Similarly, the C-C single bonds adjacent to carbonyl groups and the substituent(s) were longer than other C-C bonds. This observation was consistent with greater delocalization of π -system electrons from bonds involving a methylene carbon atom [89].

Addition of an extra electron to PBQ changed the bond lengths and bond angles significantly. The calculated C=O bond length expanded (0.046 Å) from 1.220 to 1.266 Å and the C=C bonds of PBQ lengthened from 1.3397 to 1.371 Å in PBQ^- (by 0.031 Å). The C-C bond of PBQ contracted from 1.486 Å (in PBQ) to 1.450 Å (in PBQ^-). The results obtained in this study deviated slightly between 0.003-0.005 from the one obtained in the literature [90]. Thus, reducing any PBQ by one electron lengthened the C=O and C=C bonds, while shortening the C-C bond lengths because the LUMO which is mainly on the C=O and C=C bonds of PBQs are pi-anti bonding orbitals (π^*) while the C-C single bonds are characterized by π -bonding orbitals and the extra electron enters the LUMO of the π^* -type orbital [49], [75], [90].

The bond lengths changes have been confirmed by the corresponding electron densities measured at the Bond Critical Point (BCP) of the bonds by electron spin density distribution of anions [49] and Fukui Function (predictor of the preferential sites to bind an electron in quinone system) [81]. In PBQ, the preferential sites to receive an electron were found to lie on oxygen and carbon atoms, but the dominant part was on the oxygen atoms, and this was justified by the shortening of the C-C bonds. The resonance effects present in PBQ also causes the elongation of the C=O and C=C bonds and shortens the C-C bonds. Substituents significantly influenced the bond length of the carbonyl groups. Addition of a substituents further weakened or removed the contribution of these original resonances [91]. There were two types of resonance mechanisms that explained changes brought by substituents on quinone molecules. The first one was the internal hydrogen bonding between the substituent hydrogen and the carbonyl oxygen, and the second one

was the interaction of the substituent p-orbital with the delocalized π system of PBQ molecule [92].

Examining the bond lengths in 2-methyl PBQ⁻, and 2-tert-butyl PBQ⁻, the effect of asymmetric substituent resulted in inequivalence between the adjacent C=O and distal C=O bonds. The bond length of the adjacent C=O was greater than that of the distal C=O bond. The bond lengths difference between these two carbonyls were 0.001 Å and 0.003 Å in 2-methyl PBQ and 2-tert-butyl PBQ, respectively. The force constant for the adjacent C=O bond was found to be less than that of the distal C=O bond in 2-methyl PBQ [92]. This indeed proved that the bond strength of the adjacent C=O was weaker than that of the distal C=O bond. Furthermore, the bond length difference between two carbonyls increased as the number of methyl groups attached to PBQ increased. It has been discovered previously that the changes induced by methyl group in the neutral state resulted from the relationship between resonance mechanism and hydrogen bonding interaction between the methyl hydrogen and the carbonyl group [74]. Upon reduction to anions, the unpaired electrons in PBQ molecules were localised in the antibonding, π^* orbital preferentially on the adjacent C=O bond and this caused the bond length to weaken. In addition, the weakening of the adjacent C=O bond was also due to steric effect between the methyl/ tert-butyl substituents with the carbonyl group adjacent to the substituent. This sterical interactions could also be used to explain the observed increase of the adjacent C=O bond length in 2,6-dimethoxy PBQ. Likewise, the C=C bonds also showed a significant increase upon attachment of an electron by 2-methyl PBQ, 2-tert-butyl PBQ and 2,6-dimethoxy PBQ. Besides the inequivalence of C=O bonds when PBQ⁻ is asymmetrically substituted, it was evident that C-C single bonds adjacent to the substituents were longer than other single bonds. During reduction, the substituents localized the unpaired electrons in the antibonding π^* orbital on the carbonyl group adjacent to the substituent, and for this reason the bond strength of C-C adjacent to the substituent and the carbonyl group in 2-methyl PBQ and 2-tert-butyl PBQ decreased, and this elongated the bond lengths. This was also notable in 2,6-dimethoxy PBQ where C-C adjacent to the substituents and the carbonyl group were longer than other C-C single bonds. The significant weakening of the adjacent C=O by introducing internal hydrogen bonding when compared to PBQ seemed to stabilize resonance structures.

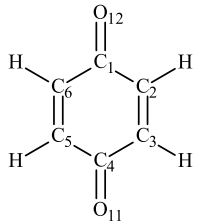
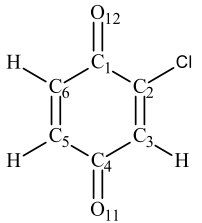
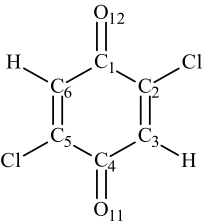
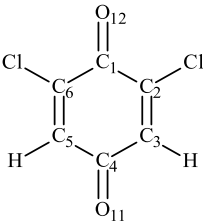
In comparison to asymmetric substitution, symmetrically substituted 2,5-dimethyl PBQ showed that both the C=O and C=C bonds were equal while the C-C bonds adjacent to the substituent and the carbonyl group were longer than other single bonds. This observation was anticipated because the methyl groups were attached to C-2 and C-5 in the ring and upon reduction, as stated above, the steric effect caused by substituents plays a major role in weakening C-C bonds adjacent to the substituent. Also, C=O and C=C bonds adjacent to the substituent will feel more effect than distal bonds and in this case, they were all adjacent to the substituents hence showing equal values [49], [74], [92]. Duroquinone on the other hand showed an anomalous behaviour. The C=O bond lengths were not equal as expected since it is symmetrically substituted. This means that there is a preferential site to bind an extra electron, which is probably around the C₁=O₁₂ in duroquinone (refer to **Table 4.13** see position of C₁=O₁₂ in duroquinone).

The optimized parameters, i.e., bond lengths and bond angles of PBQ and electron withdrawing derivatives of PBQs together with their anions computed using B3LYP with the 6-311G++(d,p) basis set are presented in **Table 4.14**. From the table, it is seen that upon substitution of the neutral PBQ molecule by an electron withdrawing group, the C=O adjacent to the substituents were longer while the C=C bonds remained the same. For example, in 2-chloro, and 2,6-dichloro PBQs, the adjacent C=O bond was longer and weaker than the distal C=O while in 2,5-dichloro PBQ and tetrafluoro PBQs they were equal. Similarly, the C-C single bonds adjacent to carbonyl groups and substituents were longer while other C-C bonds either remains the same or decreased by 0.01 Å.

Reducing halogenated PBQs by one electron increased the C=O and C=C bond lengths while reducing their C-C single bonds. Comparing 2,5-dichloro PBQ⁻ (1.25 Å) and 2,6-dichloro PBQ⁻ (1.24 Å), the C=O bond adjacent to the substituent became shorter in 2,6-dichloro PBQ⁻ whereas in 2,5-dichloro PBQ⁻ they were the same. Similarly, the C-C bond lengths shortened by either 0.003 or 0.004 Å from neutral molecule to molecular anions, but addition of halogens to PBQ⁻ increased the C-C bonds adjacent to the substituents while other C-C bonds remained unchanged together with those in tetrafluoro PBQ⁻. The contraction of the C=O bonds and expansion of C-C bonds in electron withdrawing derivatives of PBQs' indicated localization of π -electrons hence bringing stability to

PBQ⁻. In general, addition of an electron to neutral molecules of PBQs weakened the C=O, C=C and C-X (X = Cl, F) bonds while the C-C single bonds became stronger [49].

Table 4.14: Geometrical parameters of PBQ and its electron withdrawing derivatives with their anions calculated using B3LYP /6-311G++(d,p)

Structural parameter (<i>bond length, Å and bond angle, °</i>)												
	neutral	anion	Δ	neutral	anion	Δ	neutral	anion	Δ	neutral	anion	Δ
C1=O ₁₂	1.22	1.27	0.05	1.21	1.26	0.05	1.21	1.25	0.04	1.20	1.24	0.04
C4=O ₁₁	1.22	1.27	0.05	1.22	1.26	0.04	1.21	1.25	0.04	1.22	1.26	0.04
C2=C ₃	1.34	1.37	0.03	1.34	1.37	0.03	1.34	1.36	0.02	1.34	1.36	0.02
C5=C ₆	1.34	1.37	0.03	1.34	1.37	0.03	1.34	1.36	0.02	1.34	1.36	0.02
C1-C ₂	1.49	1.45	-0.04	1.50	1.46	-0.04	1.50	1.46	-0.04	1.50	1.46	-0.04
C1-C ₆	1.49	1.45	-0.04	1.49	1.45	-0.04	1.48	1.45	-0.03	1.50	1.45	-0.05
C4-C ₅	1.49	1.45	-0.04	1.49	1.45	-0.04	1.50	1.46	-0.04	1.48	1.45	-0.03
C3-C ₄	1.49	1.45	-0.04	1.48	1.45	-0.03	1.48	1.45	-0.03	1.48	1.45	-0.03
C-X (X=H, Cl, F)	1.08	1.09	0.01	1.73	1.78	0.05	1.73	1.78	0.05	1.73	1.77	0.04
C ₆ -C ₁ -C ₂	117.3	114.8	-2.5	117.6	115.0	-2.6	116.5	113.4	-3.1	115.3	116.7	1.4
C ₃ -C ₄ -C ₅	117.3	114.8	-2.5	116.2	113.0	-3.2	116.5	113.4	-3.1	118.0	115.4	-3.4
C ₁ -C ₂ =C ₃	121.3	122.6	1.3	121.6	124.0	3.6	121.4	123.6	2.2	122.7	124.9	2.2
C ₄ -C ₅ =C ₆	121.3	122.6	1.3	121.2	122.2	1.0	121.4	123.6	2.2	121.0	121.6	0.6

4.3.6 Substituent effect on the vibrational spectra of PBQs

The vibrational frequency shifts can be associated with the level of charge transfer, and it normally show the presence and strength of intermolecular interactions i.e., internal hydrogen bonding between the substituent hydrogen (in the case of methyl substituents) and the carbonyl oxygen, and the interaction of the substituent p-orbital with the delocalized π -system of the quinone [92]. The nature and extent of these interactions mainly affect the structure of quinones and their molecular radical anions. In this context it was relevant to understand how the structural changes of PBQs and their molecular radical anion were influenced by the substitution.

4.3.6.1 C=O stretching vibrational frequencies

The most prominent feature on the vibrational spectra of PBQs was the C=O stretching mode, therefore the main focus was directed towards understanding the influence brought by the presence and orientation of substituents on the carbonyl stretching mode of PBQs and their molecular radical anions. The theoretical and experimental [93], [94] infrared spectra of PBQ and 2-methyl PBQ in C=O stretching region are shown in **Figure 4.17** and **Figure 4.18** respectively. There is fairly good agreement between theoretical and experimental spectra.

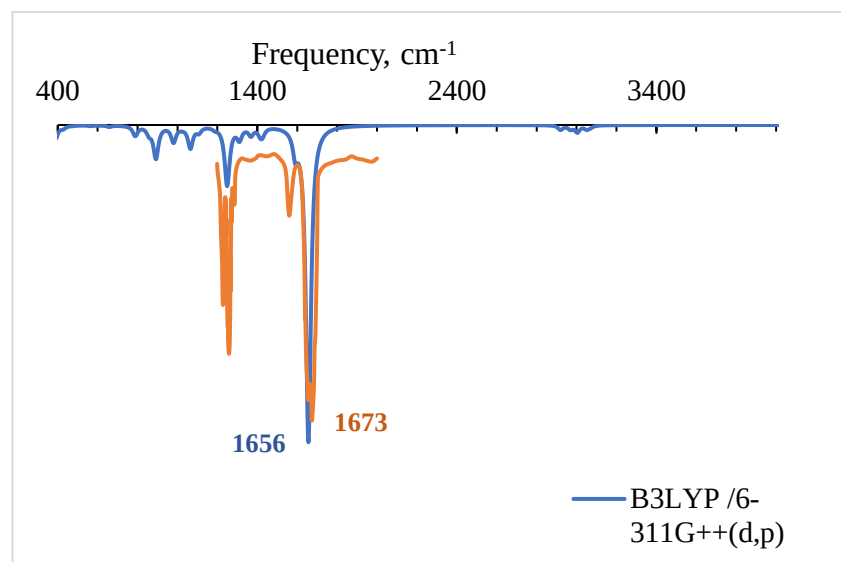


Figure 4.17: The theoretical and experimental, [93] Infrared spectrum of PBQ in the C=O stretching region. *Note; Theoretical data has been scaled by 0.97 scaling factor previously determined [95] to obtain the best agreement with the experimental data.*

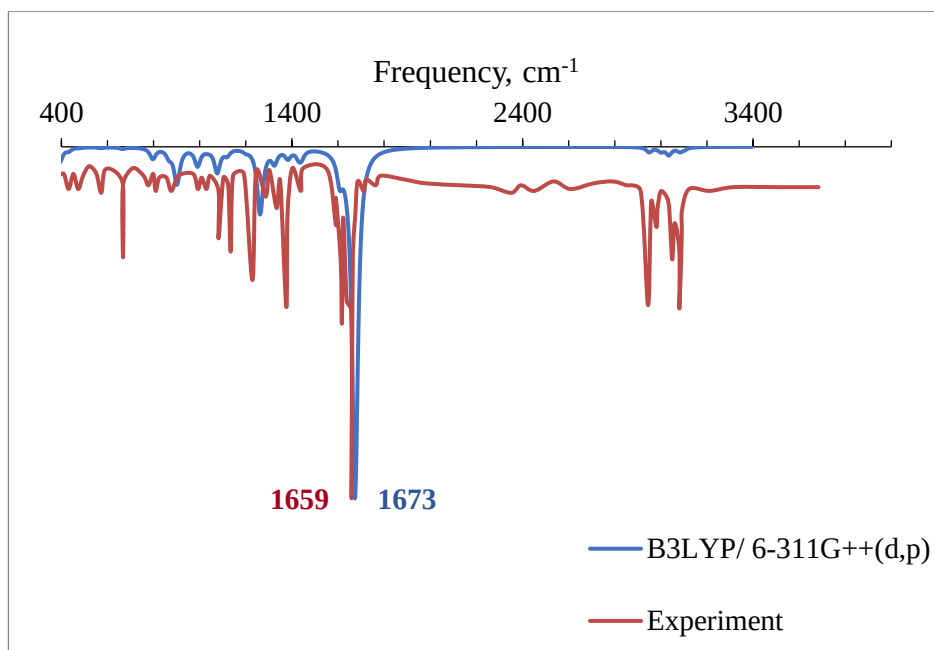


Figure 4.18: The theoretical and experimental [94] infrared spectrum of 2-methyl PBQ in the C=O stretching region. *Note; Theoretical data has been scaled by 0.97 scaling factor previously determined [95] to obtain the best agreement with the experimental data.*

Comparing measured vibrational frequency for the neutral molecule with corresponding mode for anion in **Figure 4.19** provided an understanding about the changes in chemical bonding when an extra electron is added to PBQ. The C=O stretching frequency for PBQ was 1728 cm^{-1} and for the PBQ anion it was 1527 cm^{-1} , a decrease of 201 cm^{-1} , which indicates that the C=O bond was significantly weaker in the molecular anion. This observation was also reflected even when the PBQ was substituted, as shown in **Table 4.15**, and it was consistent with previous studies [92].

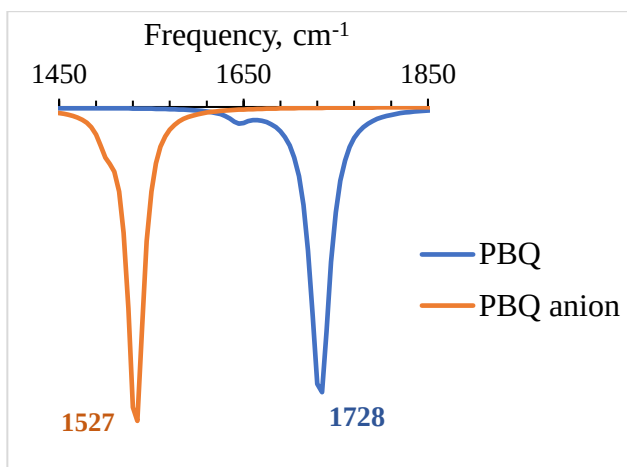


Figure 4.19: Infrared spectrum of PBQ and PBQ⁻ in the C=O stretching region calculated using B3LYP /6-311G++(d, p).

Table 4.15: The C=O stretching vibrational mode and frequencies, cm⁻¹ of PBQs and their corresponding anions calculated using B3LYP /6-311G++(d, p).

Molecule	Frequency, cm ⁻¹ (intensity)	
	Neutral	Anion
PBQ	1728 (s)	1527 (s)
2-methyl PBQ	1721 (s), 1725 (w)	1525 (s), 1526 (m)
2,5-dimethyl PBQ	1717 (s)	1520 (s)
Duroquinone	1699 (s), 1706 (w)	1496 (w), 1506 (s)
2-tert-butyl PBQ	1716 (s), 1720 (s)	1477 (w), 1522 (s)
2,6-dimethoxy PBQ	1694 (s), 1768 (s)	1535 (s), 1633 (m)
2-chloro PBQ	1723(s), 1744 (s)	1503 (w), 1535 (s)
2,5-dichloro PBQ	1742 (s)	1539 (s)
2,6-dichloro PBQ	1716 (s), 1764 (vs)	1513 (m), 1548 (s)
Tetrafluoro PBQ	1760 (s)	1549 (s)

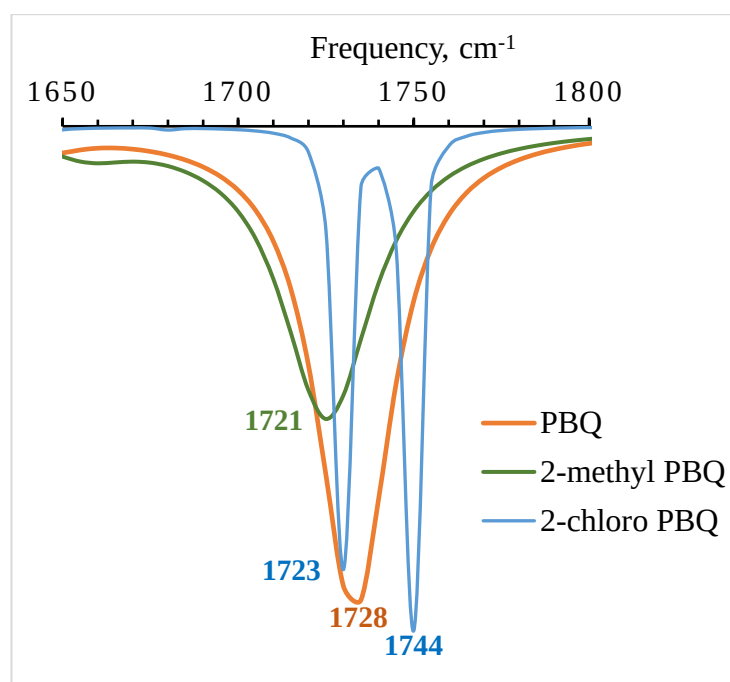


Figure 4.20: Infrared spectra showing effects of substituents on the C=O vibrational mode of PBQ calculated using B3LYP /6-311G++(d, p).

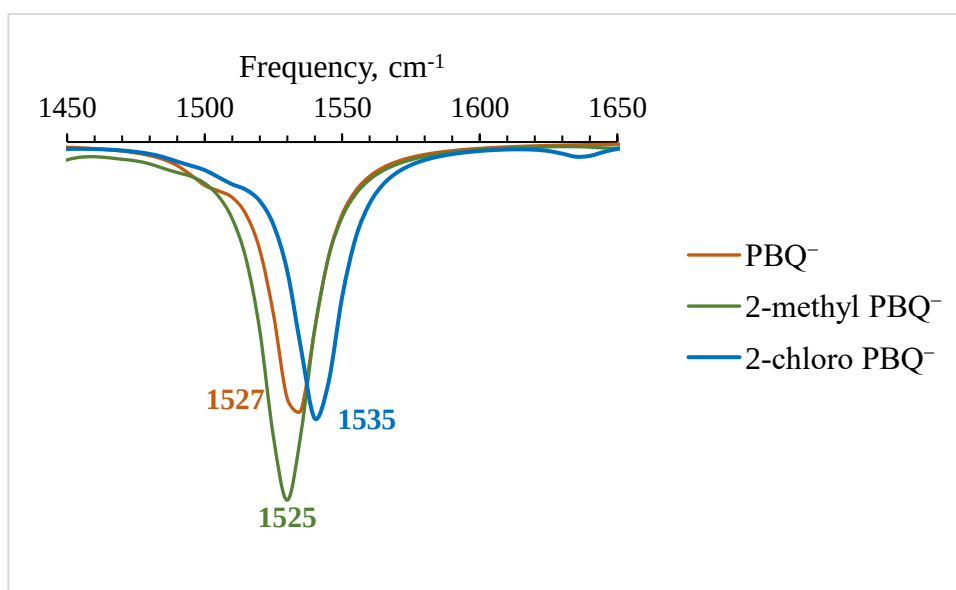


Figure 4.21: Infrared spectra showing effects of substituents on the C=O vibrational mode of PBQ anion calculated using B3LYP /6-311G++(d, p).

The most significant difference reflected in **Table 4.15** which was clearly displayed in **Figure 4.20** and **Figure 4.21** was that electron donating substituents reduced the C=O frequency of PBQ and its molecular anion while electron withdrawing substituents

increased it. Symmetrically substituted PBQ anions (2,5-dimethyl PBQ⁻, 2,5-dichloro PBQ⁻ and tetrafluoro PBQ⁻) exhibited only one band in that region as it was with unsubstituted PBQ anion unlike the unsymmetrically substituted PBQ anions (2-methyl PBQ⁻, 2-tert-butyl PBQ⁻, 2-chloro PBQ, 2,6-dimethoxy PBQ and 2,6-dichloro PBQ⁻) which showed two distinct bands.

Figure 4.21 shows a low resolution between the two peaks of 2-methyl PBQ anion. As indicated in **Table 4.15** the two bands in 1525 and 1526 cm⁻¹ had reduced separation and this led to overlapping to an extent that prevented resolution of the individual peaks. Our calculation predicted the C=O bond adjacent to the methyl group vibrated at a higher frequency compared to distal C=O bond. In 2,5-dimethyl PBQ only one C=O vibration at 1520 cm⁻¹ occurred because the C=O groups in this case were chemically equivalent. Vibrations at 1496 and 1506 cm⁻¹ were found when four methyl groups were added to PBQ anion. The antisymmetric and symmetric C=O modes occurred at 1496 and 1506 cm⁻¹, respectively. Similarly, 2-tert-butyl PBQ anion produced two bands at 1477 and 1522 cm⁻¹ where C=O adjacent to tert-butyl group appeared at higher frequencies. In 2,6-dimethoxy PBQ anion, the C=O bands occurred at 1535 and 1633 cm⁻¹. The band at 1694cm⁻¹ corresponded to the C=O adjacent to the methoxy groups.

Introducing Cl atom to PBQ anion produced two carbonyl bands shifted to higher frequencies from 1527 cm⁻¹ in PBQ anion. These peaks had a low resolution in **Figure 4.21** but **Table 4.15** clearly present that absorption bands in 1503 and 1535 cm⁻¹ correspond to these peaks. Note a good resolution between these peaks in **Figure 4.20** where the substitution was on PBQ neutral molecule. The higher frequency was due to the anti-symmetric stretch, which mainly involved the C=O adjacent to the Cl atom. This positive shift was observed previously [96], where it was clearly noted that the positive shift was due to the dipolar effect of Cl atom. The introduction of another Cl atom adjacent to the second carbonyl (C=5) produced a single intense band at 1539 cm⁻¹ but when the second Cl atom was introduced to C=6, as in 2,6-dichloro PBQ anion, two carbonyl bands which were 35 cm⁻¹ apart were formed. This separation was 13 cm⁻¹ less

than the one observed in 2,6-dichloro PBQ neutral molecule. Lastly, tetrafluoro PBQ anion as expected, showed a single intense carbonyl band at 1549 cm^{-1} .

Previous studies [96], [97], have revealed the mesomeric effect introduced by the electron donating substituent to the distal C=O which seemed to shift the vibrational mode to lower frequencies. The steric and inductive effects induced by electron withdrawing substituents shifted the vibrational mode of the adjacent C=O to higher frequencies. In symmetrically substituted PBQs, the contribution of the steric effect was diminished.

4.3.6.2 Other fundamental vibrational modes observed in the fingerprint region

Our calculation revealed infrared active vibrations at between 400 and 1500 cm^{-1} . In neutral species, the modes between 1250 - 1300 cm^{-1} corresponded to combination of C-C stretching's of $C_{\text{ring}}\text{-}C_{\text{ring}}$ and $C_{\text{ring}}\text{-CH}_3$ bonds. In 2-chloro-, 2,5-dichloro- 2,6-dichloro- and tetrafluoro PBQs, strong bands corresponding to C-X (X=Cl, F) stretching mode occurred at 999 , 1022 , 784 and 1322 cm^{-1} respectively. In addition to the C-X stretch mode, halogenated PBQs also showed strong bands which were assigned to C-C-C bending mode, e.g., the band at 1284 cm^{-1} in 2-chloro PBQ, 1205 cm^{-1} in 2,5-dichloro PBQ and 1323 cm^{-1} in tetrafluoro PBQ. As for 2,6-dichloro PBQ, there were two significant bands at 1035 cm^{-1} 1278 cm^{-1} (see **Appendix I**) which correspond to both the bending mode of C-C-C adjacent to the two Cl atoms and C-H bending mode for each case. Upon reduction to form corresponding anionic species, the vibrational frequencies for all these modes shifted to lower frequencies.

5 CONCLUSION

The aim of this study was to investigate the effect of substituents on the stability and fragmentation of para-benzoquinone molecular anion, and it was hypothesised that substituents have a major effect on the molecular properties of PBQ and as a result they affect the stability and fragmentation of the molecular anion, and this hypothesis was well verified. Electron donating substituents decreased the stability of the molecular anion and led to the formation of more anion fragments under electron capture negative chemical ionisation mass spectrometry conditions while electron withdrawing substituents showed the opposite effect.

The theoretical fragmentation schemes constructed for all dissociation channels in all molecules speculate that most of the fragment anions were formed due to loss of CO and/or C₂H₄ from the molecular anions, sometimes accompanied by migration of H-atom to a nearby or distant C-atom or elimination of H-atom/s. Methylated PBQs retained several features of the spectra of PBQ itself. In addition to the pronounced molecular anion peaks and [M-CO]⁻, there were other significant peaks at *m/z* 41, 53, 54, 55, 80 and 81 corresponding to the formation of [C₂HO]⁻, [C₃HO]⁻, [C₃H₂O]⁻, [C₃H₃O]⁻, [C₅H₄O/ C₄O₂]⁻ and [C₄HO₂]⁻ respectively. Similar to methylated PBQs 2,6-dimethoxy PBQ also showed the formation of [C₂HO]⁻ and [M-CO]⁻ fragments, in addition to [OCH₃]⁻, [M-(OCH₂ + CH₃)]⁻, [M-OCH₃]⁻ and [M-CH₃]⁻. Unlike electron donating derivatives, electron withdrawing derivative's base peaks were due to Cl⁻ or F⁻. The most common fragment anions apart from Cl⁻ in chlorinated PBQs at *m/z* 41, 53 and 80 corresponds to [C₂HO]⁻, [C₃HO]⁻, and [C₄O₂]⁻, respectively.

Electron affinities, reduction potentials, geometrical parameters, and the C=O stretching frequencies were also affected by substituents. Electron donating substituents decreased the electron affinity and reduction potentials, hence destabilizing the molecular anion. Electron withdrawing substituents on the other hand, help stabilize the negative charge of the reduced PBQ, as a result, the electron affinity and reduction potential increases. The destabilization of molecular anions by methyl substituents on sp²- hybridized carbon is

the reason why they extensively fragment when compared to halogen substituents. An additional methyl group in the system drastically decreases the intensity of the molecular anion, while an additional halogen increases it.

Electron donating substituents also increase the C=O and C=C bond lengths of both the neutral and molecular anion of PBQ, whereas electron withdrawing substituents decrease them. Upon addition of an extra electron, there is significant increase of the C=O adjacent to the substituents. The contraction of the carbonyl bonds in electron withdrawing derivatives indicate localized π -electrons which brings stability to PBQ^- . The weakening of the C=O bond following reduction to the anion is consistent with the downshift of the calculated symmetric and asymmetric C=O bond stretching frequency. Electron withdrawing substituents increase the C=O frequency while the electron donating substituents reduce it. The inductive effect in electron withdrawing groups decrease the ionic character of the C=O bond while electron donating groups increases it. In asymmetrically substitution with respect to C=O bond, the frequency of the adjacent C=O is found at higher frequency than that of distal C=O.

In a nutshell, electron withdrawing substituents help in stabilizing the molecular anion of PBQ by dispersing the negative charge while electron donating substituents have a destabilizing effect on PBQ molecular anion because they tend to release electrons towards the ring conjugated system, and this increased the electron density within the ring, hence the reason why the mass spectra of PBQs with electron donating groups show many fragmental peaks and low intensities of the molecular anions (>10 000 ion counts) as compared to those with electron withdrawing groups with fewer fragmental anions and high intensities of the molecular anion (<10 000 ion counts).

6 RECOMMENDATIONS FOR FUTURE RESEARCH

To improve the findings of this research, the following recommendations are suggested for future research;

First, as noted in the discussion, the agreement between the experimental and theoretical mass spectra is not good. The reason for this is that the tight-binding semi-empirical method (GFN-xTB) is suitable for positive ion mass spectra and not negative ion mass spectra. Dissociative electron attachment in Quantum Chemistry Electron Ionization Mass Spectrometry (QCEIMS) calculations should ideally be performed using *ab initio* molecular dynamics (AIMD) such as with density functional theory or wave function based methods. Although stationary single molecule *ab initio* methods are feasible even with laptop computers, for molecular dynamics calculations, these need significant computational resources and could not be performed in this study.

With regards to experiments, there is a need to expand the types of electron withdrawing and electron donating substituents in order to gain more insight into the effects of different substituents. The effect of nitrogen based electron withdrawing groups such as $-\text{CN}$ and $-\text{NO}_2$ can be investigated. Other potential donating groups include $-\text{NH}_2$ and OR groups.

Electrochemical measurements in this research were performed on benzoquinones dissolved in acetonitrile, which is a polar aprotic solvent. It is known that solvents affect electrochemical reduction potentials [61]. Other solvents may also be used as these may interact with the reduced and oxidised form of benzoquinones differently. Both polar-protic and non-polar solvents could be used for further studies.

Finally, the observed stability of duroquinone molecular anion and its strong signal response in the mass spectrum shows that it is potentially a good electron scavenger. For example, it may be applied in photo-catalysis for the direct determination of the formation rate of electrons produced by excitation of a photo-catalyst.

7 REFERENCES

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8 APPENDIX I: VIBRATIONAL FREQUENCIES OF PBQs

<i>Frequency, cm⁻¹ and (relative intensity, %)</i>				
Molecule	Neutral		Anion	
PBQ	90.0 (w)	C=O w	127.9 (w)	C=O w
	413.2 (w)	C=O b	389.9 (w)	C=O b
	512.5 (w)	In-plane ring (d)	511.9 (w)	C-H w
	901.1 (w)	C-H w	790.2 (w)	C-C-C ss
	1082.5 (w)	C-H b	850.2 (w)	Ring breathing, C-H w
	1312.6 (w)	C-C-C as, C-H b	960.6 (w)	C-C-C ss, C-H b
	1641.2 (w)	C=C ss	1073.9 (w)	C-C-C as, C-H b
	1728.4 (s)	C=O ss, C-H b	1218.5 (w)	C-C-C as, C-H b
	3192.5 (w)	H-C=C-H ss0	1366.2 (w)	C=O ss, C-H b
			1494.3 (w)	C-H b, C=C ss
			1527.1 (s)	C=O ss
			3124.4 (w)	C-H ss
			3145.2 (w)	C-H ss
2-methyl PBQ	82 (w)	Ring torsion	120.9 (1.8)	C=O w
	400.5 (w)	C=O b	381.7 (w)	C=O b
	815.9 (w)	C-H w	794.5 (w)	C-C-C s, C-H b
	923.6 (w)	C-H w	874.4 (w)	C-H w
	1017 (w)	C-H _(Me) b, C-C s	1010.5 (w)	C-H _(Me) b, C-C s
	1105.1 (w)	C-H b	1150.7 (w)	C-C s, C-H b
	1296.6 (m)	C-C-C as, C-H b	1351 (3w)	C-C s, C-H b
	1359.6 (w)	C-C-C as, C-H b	1433.1 (w)	C-C-C as, C-H b
	1418.3 (w)	C-H (Me) w	1525.3 (s)	C=O s, C-C-C s, C-H b
	1479.5 (w)	C-H _(Me) b	1526.2 (s)	C=C s, C=O s, C-H b
	1650.6 (w)	C=C s, C-H b	3005.6 (w)	C-H _(Me) s
	1721.1 (s)	C=O s, C=C s, C-H b	3047.6 (w)	H-C-H _(Me) as
	1725.1 (m)	C=O s	3125.3 (s)	C-H s
	3123.2 (w)	C-H _(Me) as	3127.3 (s)	C-H as
			3150.7 (w)	C-H s
2,5- dimethyl PBQ	402.9 (w)	C=O b, C-H _(Me) b	708.8 (w)	C-H _(Me) w, C-CH ₃ s
	932.7 (w)	C-H w	886.6 (w)	C-H w
	1016.7 (w)	C-H b	1005.8 (w)	C-H b
	1170.6 (w)	C-CH ₃ s, C-H b	1157.4 (w)	C-H b, C-C s
	1258.6 (w)	C-C-C as, C-H b	1203.1 (w)	C-C-C as, C-H b
	1360.8 (w)	C-H b, C-C-CH ₃ as	1474.7 (w)	C-H (Me) b
	1416.0 (w)	C-H (Me) w	1520.0 (s)	C=O s, C-H _(Me) b
	1480.2 (w)	C-H (Me) b	1542.1 (w)	C=C s, C-H b
	1663.2 (w)	C=C s, C-C-CH ₃ s	3003.5 (m)	C-H _(Me) s
	1716.6 (s)	C=O s, C-C-C s	3045.5 (w)	C-H as
	3122.1 (w)	C-H s, C-H as	3073.6 (w)	C-H as, C-H s
			3123.3 (w)	C-H s

duroquinone	56.4 (w) 434.3 (w) 716.9 (w) 871.4 (w) 1053.6 (w) 1140.3 (w) 1148.8 (w) 1294.6 (m) 1407.0(w) 1489.5 (w) 1662.6(w) 1698.5 (s) 1706.0 (w) 3032.6 (w) 3080.1 (w) 3139.3 (w)	C=O w, C-CH ₃ w, C-H b C=O b C-H b, C-C-C s CH ₃ -C s C-CH ₃ b C-C-C s, C-H b C-C-C b, C-H b C-C-C s, C-H b C-H w C-H b C=C s, C-H b C=O s, C=C s C=O as C-H s C-H as C-H as, C-H s	89.8 (w) 415.0 (w) 613.4 (w) 1096.1 (w) 1126.4 (w) 1226.5 (w) 1298.6 (w) 1377.2 (w) 1396.6 (w) 1466.7 (w) 1491.5 (w) 1496.3 (w) 1506.2 (m) 1544.9 (w) 2999.7 (m) 3025.7 (w) 3101.3 (w)	C=O w, C-CH ₃ w, C-H b C=O b C-C-C b, C-CH ₃ as C-C-C as, C-H b C-C-C s, C-H b C-C-C s, C-H b C-C-C s, C-H w C-C-C s, C-H w C-H w C-H b C-H b C=O s, C-H b C=O s, C-H b, C-C-C s C=C s, C-C-C as, C-H b C-H s H-C-H as H-C-H as, H-C-H s
2-tert butyl PBQ	436.7(w) 849.8 (w) 942.4 (w) 1020.1 (w) 1116.1 (w) 1269.4 (w) 1299.2 (w) 1350.3 (w) 1397.9 (w) 1502.8 (w) 1525.3 (w) 1715.7 (s) 1720.0 (m) 3023.6 (w) 3025.5 (w) 3032.0 (w) 3084.2 (w) 3091.0 (w) 3096.0 (w)	C=O w C-H w C-H w C-C s, C-H b C-H b C-H b, C-C(CH ₃) ₃ s C-C-C b, C-H b C-H _(Me) w C-H _(Me) b C-H _(Me) b C=C s, C-H C=C s, C=O s C=O s, C=C s C-H _(Me) s C-H _(Me) s C-H _(Me) s C-H _(Me) as C-H _(Me) as C-H _(Me) as, C-H _(Me) s	813.5 (w) 824.0 (w) 890.3 (w) 1029.6 (w) 1057.6 (w) 1266.8 (w) 1342.3 (w) 1405.9 (w) 1428.4 (w) 1476.7 (w) 1508.5 (w) 1521.8 (s) 1532.0 (w) 2988.8 (w) 2994.5 (m) 3010.3 (m) 3015.3 (w) 3052.8 (w) 3065.9 (w) 3080.6 (w) 3129.8 (w) 3152.6 (w)	ring b, C-C s C-H w C-H w C-C(CH ₃) ₃ t, C-C s C-H b C-C(CH ₃) ₃ s, C-H b C-H (Ring) b C-H _(Me) w C-C-C as, C-H b C=O s, C=C s, C-H b C=C s, C=O s C=O s, C=C s C-H _(Me) b C-H _(Me) s C-H _(Me) s C-H _(Me) s C-H _(Me) as C-H _(Me) as C-H _(Me) as, C-H _(Me) s C-H _(Me) as C-H as C-H s
2,6-dimethoxy PBQ	871.1 (w) 1037.6 (w) 1128.0 (s) 1236.9 (s) 1282.5 (m) 1327.2 (m) 1339.9 (m) 1493.2 (w) 1499.6 (w) 1630.2(s)	C-H w O-CH ₃ s O-CH ₃ s, C-C-C as C-O-CH ₃ as C-C-C s, C-H b C-C-C as, C-H b C-C-C s, C-H b C-H _(Me) b C-H _(Me) b C=C as C=C as	819.5 (w) 1068.5 (w) 1145.4 (m) 1178.9 (m) 1190.3 (s) 1214.9 (m) 1428.7 (m) 1504.4 (w) 1519.6 (w) 1534.7 (s)	C-H w O-CH ₃ s C-C-C as, C-O-CH ₃ s C-C-C as, C-H b C-C-C s, C-H b C-H _(Me) w C-C-C as, C-H b C-H _(Me) b C=C as C=O s

	1680.5 (w) 1693.8 (s) 1768 (m) 3019.9 (w) 3085.3 (w)	C=C s C=O s C=O s C-H _(Me) s H-C-H _(Me) as	1633.0 (m) 2973.8 (m) 3018.4 (w) 3090.8 (w) 3184.5 (w)	C=O s C-H _(Me) s C-H _(Me) as C-H _(Me) s C-H s
2-chloro PBQ	431.4 (w) 917.4 (w) 998.9 (m) 1109.7 (w) 1284.3 (m) 1320.9 (w) 1628.8 (m) 1723.0 (s) 1744.0 (s)	C=O b C-H w C-Cl s C-H b C-H b, C-C-C as C-H b C=C stretch C=O stretch C=O stretch	810.4 (w) 867.4 (w) 989.8 (m) 1196.0 (w) 1333.6 (w) 1502.7 (w) 1535.0 (s) 1633.4 (w) 3136.0 (w) 3157.8 (w)	C-H b C-H w C-Cl s C-H b C-H b C=O s C=O s, C=C s C=C s C-H as C-H s
2,5-dichloro PBQ	591.3 (w) 802.8 (w) 918.3 (w) 1022.3 (s) 1206.3 (w) 1625.9 (m) 1742.3 (s)	C=O w C-C-C s, C-H b C-H w C-Cl s C-C-C s, C-H b C=C s C=O s	557.3 (w) 829.5 (w) 874.1 (w) 1006.7 (m) 1290.8 (w) 1539.4 (s)	C=O w C-C-C s, C-H b C-H w C-Cl s C-H b C=O s, C=C s
2,6-dichloro PBQ	443.9 (w) 783.6 (m) 919.3 (w) 1034.5 (m) 1277.9 (s) 1292.3 (w) 1624.4 (m) 1665.4 (w) 1716.0 (s) 1764.8 (s)	C-H b, C=O b C-Cl s C-H w C-H b, C-C-C s C-C-C as, C-H b C-H b, C-C s C=C as C=C s C=O s C=O s	450.1 (w) 752.8 (m) 816.2 (w) 866.6 (w) 915.0 (w) 1017.9 (w) 1112.9 (w) 1512.6 (m) 1548.3 (s) 1623.8 (w)	C-H b, C=O b C-Cl s C-C-C s, C-H b C-H w C-C=C s, C-Cl C-H b, C-C-C s C-C-C as, C-H b C=O s C=O s C=C
tetrafluoro PBQ	214.0 (w) 1001.5 (s) 1322.8 (s) 1699.5 (s) 1760.0 (s)	C-F w, C=O w Ring vibration s C-C-C s, C-F s C=C s C=O s	963.7 (m) 1046.6 (m) 1213.3 (m) 1301.5 (m) 1548.8 (s) 1574.1 (m)	Ring vibration C-C-C s, C-F s C-C-C as C-C-C s, ring deformation C=O s C=C s